

PROCEEDINGS  
OF THE  
NATIONAL ACADEMY OF SCIENCES  
INDIA

1955

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VOLUME 24

SECTION—A

PART I

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PROCEEDINGS  
OF  
THE SYMPOSIUM  
ON  
RECENT TRENDS IN SOIL  
RESEARCH

PART I

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PROCEEDINGS  
OF  
THE SYMPOSIUM  
ON  
RECENT TRENDS IN SOIL RESEARCH  
HELD DURING  
THE TWENTY-FOURTH ANNUAL SESSION  
OF  
THE NATIONAL ACADEMY OF SCIENCES, INDIA  
AT  
THE UNIVERSITY OF SAUGAR, SAUGAR (M. P.)  
ON  
27th & 28th DECEMBER 1954  
PART I

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# PROCEEDINGS OF THE NATIONAL ACADEMY OF SCIENCES, INDIA 1955

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PART I

A Symposium on "Recent Trends in Soil Research" was held under the auspices of the National Academy of Sciences, India, during the twenty-fourth annual session on the Academy held at the University of Saugar, Saugar, on 27th & 28th December, 1954. Professor N. R. Dhar, D.Sc., (Lond. and Paris), F.R.I.C., F.N.I., F.N.A.Sc., I.E.S. (Retired), Director, Sheila Dhar Institute of Soil Science, University of Allahabad, presided over all the sessions of the Symposium. There was an unprecedented enthusiasm for the Symposium and 105 papers were received from all parts of the world. The Symposium was divided into the following sections :

1. Soil Physics.
2. Soil Mineralogy and physico-chemical properties of soils.
3. Soil Chemistry.
4. Soil Fertility.
5. Soil Microbiology.
6. Trace Elements in Soils.
7. Acid, alkali and saline soils.
8. Tropical and sub-tropical soils.
9. Soil conservation and management.
10. Land classification and evolution.

Professor N. R. Dhar in his Presidential Address discussed the nitrogen problem and improvement of land fertility by organic matter and phosphates. He discussed in detail the researches carried out by him and his co-workers for over 35 years. Professor Dhar's address was followed by the presentation of the papers. The papers of those authors who could not be present were read. Each paper was followed by lively discussion. Some of those who took part in the discussions are Prof. S. Ghosh, Dr. S. K. Mukerjee, Dr. S. K. Ghosh, Dr. S. P. Mitra, Dr. S. G. Mitra, Dr. B. Bose, Dr. K. L. Nagpal, Dr. S. Pritam Singh, Mr. Hari Shankar, Mr. Dharam Prakash, Mr. M. M. Rai, Mr. T. B. Guha Roy, Mr. T. N. Chojer, Mr. M. S. Lal, Mr. N. K. Garg, Mr. Raghunir Singh, Mr. D. Sharma, Mr. K. M.



Verma, Dr. S. K. Pal, Dr. A. K. Dey, Dr. G. H. Dungan, Mr. A. K. Ghosh, Mr. A. K. Bhattacharya, Mr. Newton Ram, Dr. M. K. Mukerjee, Dr. S. P. S. Teotia, Prof. N. V. Joshi, Mr. S. S. Singh, Dr. S. N. Banerjee, Dr. A. K. Bhattacharya, Mr. O. N. Tripathi and Mr. P. N. Avasthi.

At the end Professor Dhar summarized all the papers presented. He also thanked all those who participated in the symposium and made it such a tremendous success.

It was originally decided to print all the papers received for the Symposium in a single volume. But due to the unusually large number of papers received it is not possible to print all the papers in a single volume as it will cover about 900 pages. The papers are being printed in 6 parts of which this volume forms the first part. The Academy, however, takes no responsibility for the opinions expressed by the authors.

The Academy conveys its thanks to Professor Dhar for organizing the Symposium, to the authors of the papers and to all those who took part in the discussions and made the Symposium a complete success.

## PRESIDENTIAL ADDRESS

### THE NITROGEN PROBLEM AND IMPROVEMENT OF LAND FERTILITY BY ORGANIC MATTER AND PHOSPHATES

By N. R. DHAR

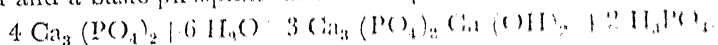
*Sheila Dhar Institute of Soil Science, University of Allahabad.*

**Inefficiency of industrial methods of nitrogen fixation.**—It is well known that the arc method of fixing atmospheric nitrogen has been completely abandoned as its efficiency never exceeded 2%. The Haber-Bosch and the Cyanamide methods of fixing atmospheric nitrogen are almost equally efficient, and, their efficiencies are not higher than 8 to 10%. Hence, the nitrogen fixing industry is making very slow progress and the cost of production of synthetic nitrogen and the market price of nitrogenous fertilizers have remained high. The European production of fixed nitrogen in 1950 was only 3% greater than its manufacture in 1938 which amounted to 3.54 million tons of fixed nitrogen. On the other hand, the production of superphosphate during the same eventful 12 years was 15% greater than the output in 1938. (Compare Fertilizer Technology and Resources in U. S. A. by Jacob 1953).

**Organic matter aided by calcium phosphates fixes atmospheric nitrogen in soil.**—Because large amounts of superphosphate, basic slag, finely divided soft phosphate rocks are being utilized in European and American agriculture, and, because, the recovery of such phosphates by crops does not usually exceed 20% of the added phosphate, a large amount of laboratory research work and field trials are going on all over the world on phosphate fixation in soils. We have discovered an important relationship between the phosphate and nitrogen status of world soils. The efficiency of nitrogen fixation in light by a mixture of organic matter and calcium phosphates can be as high as that by legumes and higher than the industrial methods. In my Presidential address to the National Academy of Sciences, India, (Business Matter, 1952, p. 15) it has been emphasised that the nitrogen status of world soils depends mostly on their calcium phosphate contents as soils rich in phosphate can also be rich in nitrogen when organic substances are added to such soils or are present therein. From extensive experiments we have come to the conclusion that the fixation of atmospheric nitrogen by the addition of organic matter to soil is greatly enhanced by the presence of calcium phosphates. (Dhar, and co-workers. Proc. National Acad. Sci. (India), 21, (1952) 137).

**Calcium Phosphate rich soils fix nitrogen by the oxidation of soil humus and have smaller C/N ratios than 10.**—Moreover, we have observed that soils rich in calcium phosphate, when allowed to undergo slow oxidation in contact with air, can fix atmospheric nitrogen by the oxidation of carbonaceous materials present in the soil humus. Also, when calcium phosphate is added to soils not rich in calcium phosphate, the fixation of atmospheric nitrogen takes place even in the absence of added organic matter. Hence, it can be concluded that soils rich in calcium phosphate or soils to which calcium phosphate is added would be richer in nitrogen and would show smaller values of C/N ratio than soils poor in calcium phosphate. It is clear, therefore, that calcium phosphate rich soils would show C/N ratio smaller than 10.

**Decomposing organic matter increases phosphate availability.**—In previous publications it has been emphasised (Dhar, Proc. National Acad. Sci., India, 27 (1952), 156; Ann. Roy. Agric. Coll. Sweden, 21, 49) that calcium phosphate in contact with water is copiously hydrolysed into free phosphoric acid and a basic phosphate as in the equation :



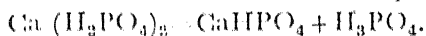
This hydrolysis is checked by the presence of calcium carbonate or lime. Hence, the amount of phosphate existing in solution from basic slag has been found to be less than that from  $\text{Ca}_3(\text{PO}_4)_2$  because basic slag is rich in lime. It has also been observed that carbonic acid converts the tri-phosphate of calcium to dicalcium phosphate and small amounts of monocalcium phosphate and, thus, the availability of phosphates of calcium and magnesium, when added to the soil along with organic matter undergoing oxidation, appreciably increases. When monocalcium phosphate is added to the soil containing organic matter there is a decrease in the available phosphate because of the conversion of the readily soluble monocalcium compound to the sparingly soluble di- or tri-calcium compound by its action on calcium carbonate of the soil. Hence, manuring by organic matter, which helps in the fixation of atmospheric nitrogen and increases available potash and phosphate is highly profitable, especially, in view of the high cost and shortage of nitrogenous fertilizers. In all our experiments as well as those carried on by other workers the solubilities of  $\text{Ca}_3(\text{PO}_4)_2$ ,  $\text{Mg}_3(\text{PO}_4)_2$ ,  $\text{CaHPO}_4$ , finely powdered rock phosphate and basic slag are appreciably increased by the presence of carbonic acid.

**Organic manuring not very profitable in acidic soils containing ferric, aluminium and titanium phosphates.**—On the other hand, our results and those of B. Lachowicz (Monatsh. 73 (1892), 357) clearly show that carbonic acid does not increase the solubility of ferric phosphate.

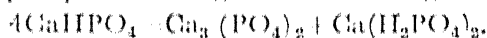
It appears, therefore, that organic manuring is not suitable in soils rich in ferric, aluminium or titanium phosphate. These compounds have to be partially converted into calcium and magnesium phosphates by the action of limestone or dolomite or free lime before organic manuring can be profitable. Experiments show that the recovery of superphosphate increases from 27 to 41.7% on liming of acid soils. Hence, in soils where large quantities of iron, aluminium or titanium phosphate are formed by adding superphosphate, as in acidic soils of Europe or America, organic manuring may be of little value and that is why people of Western Europe, where the soils are acidic and to which large quantities of superphosphate are added, have not yet appreciated organic manuring much. In tropical countries, however, where the soils are on the alkaline side and the phosphates present therein are chiefly calcium and magnesium phosphates, organic manuring with dung, straw, leaves, grasses, legumes, peat, lignite and even sawdust, mixed with large doses of calcium phosphate or basic slag, is extremely profitable, because, the mixture is conducive to maintenance of soil neutrality and increase of humus, the loss of which from soils causes infertility, alkalinity, increase of soil erosion and formation of desert conditions of land.

**Calcium—mono, di and triphosphates readily interchangeable in properties.**—A Rindell (Untersu. Löslichkeit Kalk phosphate, Helsingfors 1890) has determined the solubilities of  $\text{Ca}_3(\text{PO}_4)_2$ ,  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{CaH}_2\text{P}_2\text{O}_7$  at different temperatures. His results show that  $\text{Ca}_3(\text{PO}_4)_2$  is less soluble than  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  at 30° but more soluble than  $\text{CaH}_2\text{P}_2\text{O}_7$ . The amount of phosphate in solution from  $\text{Ca}_3(\text{PO}_4)_2$  is 1.85 millimols, from  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  it is 2.91 millimols and from  $\text{CaH}_2\text{P}_2\text{O}_7$  it is 1.22 millimols of  $\text{H}_3\text{PO}_4$  per litre. The

amounts of  $\text{H}_3\text{PO}_4$  available in solution of these phosphates change to a greater extent than those of lime with increase of temperature, but, the changes are haphazard. If the solubility of  $\text{Ca}_3(\text{PO}_4)_2$  in water is estimated by the analysis of the amounts of lime present in the dissolved condition, the solubility of  $\text{Ca}_3(\text{PO}_4)_2$  appears to be 1/20th. of that of  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  and less than 1/10th. of that present in the solution of  $\text{CaHPO}_4$ , the solubilities of lime being 0.07, 1.7 and 0.7 millimols per litre respectively. That is why earlier investigators have recorded that the solubility of dicalcium phosphate is 0.023 gram whilst that of tricalcium phosphate is 0.0013 gram at 0° per 100 grams water. But from a large amount of experiments we have come to the conclusion that tricalcium phosphate is hydrolysed to a greater extent than  $\text{CaHPO}_4$  or  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  which, when treated with water, dissolves mostly as such. The tricalcium salt in presence of water forms small amounts of phosphoric acid and monocalcium phosphate, and that is why the pH of an aqueous solution of tricalcium phosphate is slightly acidic. It is well known that monocalcium phosphate is acidic and in concentrated solutions breaks up as follows :—



Dicalcium phosphate undergoes the following change in contact with water :—



Hence, the three calcium phosphates appear to be interchangeable in their properties.

**Indian rock phosphates unsuitable for superphosphate manufacture.**—It is a pity that bones which are valuable sources of calcium phosphate are still largely exported from India. The natural Indian phosphate deposits found in Travancore and Bihar are not extensive and being rich in iron and aluminium compounds are not as suitable for superphosphate manufacture as the African or American deposits which contain small amounts of iron and aluminium.

**Indian basic slag as good as American slag and profitable for crop production in conjunction with organic matter.**—On the other hand, India possesses large amounts of basic slag produced from the expanding steel industry and these slags remain unutilised. From a large number of analyses it has been found that the Tata basic slag contains 7.3% of  $\text{P}_2\text{O}_5$  which compares favourably with the phosphate content of basic slags in the American markets. The Tata basic slags and other phosphates when used with organic matter not only fix atmospheric nitrogen and supply available phosphate and increase the crop production and improve the fertility of normal soils but also reclaim the *usar* and alkali soils permanently. The calcium phosphates not only supply the phosphate requirements of human beings, animals, plants and microorganisms but also help the oxidation processes and maintain the neutrality of living cells and tissues.

**Phosphates check loss of lime and maintain soil neutrality.**—

We have discovered that the addition of phosphates to soils checks the loss of lime markedly by leaching with rain water and thus avoids the formation of acidic soils. This happens because in all soils  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  is formed from tricalcium phosphate more readily than calcium bicarbonate by the action of carbonic acid on the calcium carbonate of soils. The dicalcium phosphate is much less soluble than calcium bicarbonate.

It has been observed that ordinarily the soil solution is poor in phosphate due to the sparing solubility of tricalcium, ferric, aluminium and perhaps titanium phosphates which are normally present in soils. Hence, a renewal of the amounts of phosphate in soil solution is absolutely necessary for crop production.

This is possible by improving the calcium phosphate status of the soils all over the world by adding large doses of powdered soft phosphate rock or basic slag which are still inexpensive. It is well known that calcium phosphate or basic slag added to leys causes a greater growth of legumes and enriches the land; but, there is no doubt that even grasses without legumes lead to considerable soil improvement by fixing atmospheric nitrogen and preserving soil nitrogen specially in presence of phosphates. Hence, adding dung or growing grass leads to land improvement. (Compare W. Davies, *The Grass Crop*, 1952, pp. 7, 256).

**Phosphates helpful in composting of plant materials by fixing atmospheric nitrogen.**—We have carried on a large number of experiments on the composting of cow-dung, wheat-straw and weeds by adding only small amounts of soil in presence or absence of powdered basic slag or rock phosphate or a mixture of superphosphate and rock phosphate. We have observed a greater fixation of atmospheric nitrogen in presence of phosphates in composting of cow-dung or wheat-straw than in their absence. Hence a mixture of superphosphate and phosphate rock or powdered bone or phosphate rock or basic slag should always be added to compost heaps to improve the value of the composts obtained.

**Reclamation of alkali land by a mixture of organic matter and calcium phosphates.**—Recently we have discovered that a mixture of *sanaï* (sann hemp) and phosphate rock or basic slag can permanently reclaim very bad alkali land. This is a very profitable and cheap method of reclaiming all alkali lands and depends on the following principle :—

The carbonic acid produced in the oxidation of *sanaï* (sann hemp) can readily convert calcium-tri-phosphate to the di-phosphate which can slowly supply calcium ions to the soil solution in small amounts, and, thus, calcium carbonate is formed by the action of the alkali present in alkali soils and the calcium ions obtained from  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ . We have also observed from our recent experiments that a mixture of organic matter and calcium carbonate is less profitable in reclaiming alkali soils than a mixture of organic matter and calcium phosphate, because,  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  is formed more readily by the action of carbonic acid on tri-calcium phosphate than the formation of calcium bicarbonate due to the action of carbonic acid on calcium carbonate. The dissociation constant of carbonic acid is larger than the 3rd, dissociation constant of phosphoric acid, and, that is why the formation of  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  is more easy than the formation of  $\text{Ca}(\text{HCO}_3)_2$ . Hence, in reclaiming alkali soils calcium phosphate is much better than calcium carbonate along with organic matter. Moreover, in the nitrification of the proteins present in legumes (like *sanaï* and *Dhanya*) nitrous and nitric acids are formed which are profitable in the reclamation of alkali land. Hence, our researches have thrown considerable light on the view point that the world food production is limited by the phosphate reserves of soils which should be copiously increased.

**Nitrogen fixation in soils by adding organic matter is mainly surface and photochemical process.**—In our experiments on nitrogen fixation by the addition of organic matter we have always observed that the numbers of total bacteria and *Azotobacter* are always greater in the dark than in the presence of light, although, the increase of total nitrogen, *i.e.*, the amount of nitrogen fixed, is always greater in light than in the dark. Exactly similar results have been obtained in the fixation of nitrogen by organic matter in presence of phosphates. Frequently, we have observed that the size of the colonies of *Azotobacter* developed on the dishes containing the soils kept in the dark is much bigger than those obtained from the dishes exposed to light. It is well known that sunlight enfeebles the microorganisms.

Russell (Soil Conditions and Plant Growth, 1932, p. 397) has stated that the approximate weight of bacterial substance in Rothamsted soil (total nitrogen is 0.256%) in top 6 inches comes to 5600 lbs/acre, and the weight of dry bacteria to 1120 lbs/acre. The total nitrogen content of bacteria 112 lbs/acre. Thus, the nitrogen in the bacteria is 1/50th. of the total weight of the bacterial population.

The average size of bacteria is approximately that of a cube of  $1/1000$  mm. size. Hence,  $1000 \times 10^6$  bacteria will weigh 1.0 gm.

The following results were obtained with cow-dung :—

*250 gm. of soil + 20 gm. of cow-dung*

EXPOSED TO SUNLIGHT

Date	Total carbon in 100 gms. of soil in gm.	Total nitrogen in 100 gms. of soil in gm.	Azotobacter count in million per gm. of dry soil.	Efficiency, i.e., amount of nitrogen fixed in mg. per gr. of carbon oxidized.
3-1-47	0.942	0.0667	2.5	...
2-2-47	0.826	0.0692	...	21.9
5-3-47	0.722	0.0714	16.0	21.7
3-4-47	0.630	0.0734	...	21.3
3-5-47	0.624	0.0736	39.0	...

COVERED

5-1-47	0.966	0.0676	2.5	...
4-2-47	0.906	0.0683	...	11.7
7-3-47	0.851	0.0690	60	12.4
5-4-47	0.800	0.0696	...	11.7
5-5-47	0.752	0.0701	115	10.4

It appears from the above tables that we have obtained an increase of  $(39 - 2.5) \times 10^6$  in the Azotobacter numbers in one gram of soil in sunlight with cow-dung and soil. Therefore, it corresponds to  $1300 \times 2240 \times 454 \times 36.5 \times 10^6$  Azotobacter per acre, supposing our soil to weigh 1300 tons per acre when 6 inches deep,

Hence, the weight of Azotobacter

$$\text{increase in lbs./acre at Allahabad} = \frac{1300 \times 2240 \times 454 \times 36.5 \times 10^6}{454 \times 10^6 \times 10^6} \\ = \frac{13 \times 224 \times 36.5}{103} = 106.29 \text{ lbs. per acre}$$

$$\text{And so the nitrogen content of the same} = \frac{106.29 \text{ lbs. per acre}}{50} = 2.13 \text{ lbs./per acre}$$

On the basis of the above calculations, the following tables have been drawn up from our experiments on nitrogen fixation using cow-dung, neem leaf or glucose D for comparing the photochemical and surface contribution of nitrogen fixation

with the bacterial one using cow-dung and neem leaf (*Melia Azadiracta*) as energy materials without adding phosphates : —

Experiments with cow-dung

No.	Condition	Gain in N in lbs./acre.	Increase in the number of Azoto- bacter per gm. of soil (in millions).	Bacterial con- tribution to total N in lbs. acre.	Photochemical and surface fixation in lbs. acre.
(a)	Exposed to light.	285.37	36.5	2.13	283.24
(b)	"	200.92	36.5	2.13	198.79
(c)	"	133.95	32.5	1.39	132.06
(a)	Covered.	90.27	132.5	7.29	82.55
(b)	"	72.80	112.5	6.55	66.25
(c)	"	58.24	105.5	6.11	52.10

Experiments with neem leaf.

No.	Condition.	Gain in N in lbs./acre.	Increase in the number of Azoto- bacter per gm. of soil (in millions).	Bacterial con- tribution to total N in lbs. acre.	Photochemical and surface fixation in lbs. acre.
(a)	Exposed to light.	308.67	29.5	1.72	306.95
(b)	"	218.40	27.5	1.60	216.80
(c)	"	107.74	25.5	1.48	106.26
(a)	Covered.	96.10	119.5	6.98	89.12
(b)	"	87.36	105.5	6.14	81.22
(c)	"	78.62	105.5	6.14	72.48

The influence of adding varying amounts of phosphates on the fixation of nitrogen by bacterial and photochemical processes using Glucose D as energy material (6.5% C) has been recorded in the following table :

Effect of phosphates ( $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ )

Treatment.	Condition.	Gain in N in lbs./acre.	Increase in the number of Azoto- bacter per gm. of soil (in millions).	Bacterial con- tribution to total N in lbs./acre.	Photochemi- cal and surface fixa- tion in lbs./acre.
No phos- phate.	Exposed	291.20	10.95	0.636	290.56
	Covered	160.16	34.00	1.980	158.08
0.5% $\text{P}_2\text{O}_5$	Exposed	355.2	12.5	0.72	354.48
	Covered	218.4	49.2	2.36	215.54
0.1% $\text{P}_2\text{O}_5$	Exposed	422.2	18.7	1.09	421.11
	Covered	218.4	52.75	3.07	215.33
0.05% $\text{P}_2\text{O}_5$	Exposed	509.60	24.9	1.45	508.15
	Covered	276.60	60.25	3.50	273.10

The foregoing calculations clearly show that in the process of nitrogen fixation the increase in the nitrogen content of the system due to increase in Azotobacter numbers (which are fixers of nitrogen) can account for an insignificant part of the increase in the total nitrogen observed in our experiments both in light and in the dark.

**Phosphates increase aminoacid synthesis by a mixture of a nitrate solution and a carbohydrate in light.**—In 1934 Dhar and Mukerji (J. Indian Chem. Soc. 11 (1934), 727) discovered that aminoacid synthesis takes place by exposing a solution of a nitrate and glucose or any other soluble energy material mixed with titania used as a photocatalyst and exposed to sunlight or artificial light. Aminoacids can be detected even after an exposure of the mixture for one hour by the well known ninhydrin test. Recently, we have carried on a large number of experiments on the synthesis of aminoacids by this method in completely sterile conditions and have observed that the aminoacids synthesised increase appreciably in presence of soluble phosphates. The aminoacids synthesised are being investigated by circular paper chromatography.

#### *Summary*

(1) The industrial methods of fixing atmospheric nitrogen are inefficient, and, hence, the cost of nitrogenous fertilizers is higher than other fertilizers.

(2) A mixture of organic substances like dung, grasses, straw, green manures, etc., with calcium phosphates can fix atmospheric nitrogen in the soil when ploughed in. The efficiency of this method of fixing atmospheric nitrogen, specially in light, is higher than the efficiency in industrial methods and can be as high as with legumes.

(3) The C/N ratios of soils rich in calcium phosphates are usually smaller than 10.

(4) The availability of phosphates always increases by the addition of organic substances which undergo oxidation in the soil. This is specially noticeable in soils containing lime.

(5) Manuring of fields by organic substances is not profitable in acidic soils containing ferric, aluminium and titanium phosphates.

(6) Mono, di and tri-calcium phosphates are readily decomposed by water and seem to be interchangeable in their properties.

(7) Chemical analyses of Indian basic slags show that they may contain 7–8%  $P_2O_5$  and are almost as good as American slags.

(8) When soluble or sparingly soluble phosphates are added to soil, the loss of lime by leaching is markedly checked and soils maintain neutrality.

(9) Calcium phosphate is helpful in composting of plant materials and can fix atmospheric nitrogen in composts.

(10) Alkali soils can be reclaimed more readily by a mixture of calcium phosphate and organic matter than a mixture of calcium carbonate and organic matter.

(11) Experimental results show that the increase of Azotobacter in the systems containing organic matter and soil with or without phosphates can explain only a very small amount of the total nitrogen increase in such systems by fixation of atmospheric nitrogen. Hence, surface and photochemical fixations of nitrogen play a very important part in such systems.

(12) A mixture of nitrate and carbohydrates aided by titania, when exposed to light, forms aminoacids readily. The amount of aminoacids synthesised in this way increases considerably in presence of soluble phosphates.



## SECTION -1

### SOIL PHYSICS

#### BLACK SOILS—PHYSICAL PROPERTIES AS RELATED TO IRRIGABILITY OF BLACK SOILS OF NARMADA VALLEY IN MADHYA PRADESH

By R. V. TAMHANE

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&

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(Communicated by Prof. N. R. Dhar)

(Received on 11th November, 1954)

Soils of Narmada Valley belong to the deeper phase of black soils of Deccan of India. Soils of 30 to 40 feet deep are quite common in the plains of Narmada and these soils are known to be very fertile.

The Narmada Valley is situated between Vindhya and the Satpura hills and has a width of almost 20 miles but the spread of the plains is more on the southern bank of the river, while the north bank of the river is very close to the hills of Vindhya range. The Valley extends over a length of almost 200 miles up to Handia.

The soil profiles examined and selected for the laboratory test were from two districts of Madhya Pradesh namely, Hoshangabad and Jabulpore of the Narmada Valley tract and one profile from the southern most part of Bhopal State on the northern bank of the river Narmada. The districts falls into two parts—the hilly part and the valley part. The valley portion is almost under continuous wheat crop in rich black soil, whereas the district of Jabulpore being at the head of the valley is almost closed on all sides by high land except the valley floor. The eastern and central parts of the plains of the river Narmada in Hoshangabad district are covered by the alluvium consisting of thick clay. A considerable portion of the south-western corner of the district of Jabulpore is also occupied by the eastern end of the great alluvial plains of the river Narmada. The thickness of the alluvium deposits as exposed along the banks of the river usually does not exceed 100 feet depth.

Present study is a preliminary investigation to understand the inherent physical properties of these soils to judge the behaviour of such soils under perennial irrigation and therefore deals more on the physical properties of soils rather than chemical ones. Chemical and mineralogical aspects will be dealt separately in another communication.

The physical properties of soils which determine the suitability of irrigation agriculture include texture and structure of various soil horizons and specially

their relation to water-holding and water releasing capacity, permeability and adaptability to drainage and the presence or absence of salt. Many physical characteristics can be evaluated fairly well by field observations but for detail and reliable estimation of soils, field observation should be supplemented with laboratory tests on representative soil samples.

A number of profiles were examined in the Narmada plains starting from Jabulpore and going right up to Harda in Khandwa District, but only four representative profiles were selected for laboratory tests.

The soil profiles, in general, do not show any distinct horizon except when a brownish yellow layer is met with in the lower horizons. In all the soils examined the brownish horizon whenever met was very deep, nearly 9 to 10 feet below the surface. This indicates that the soils are of deeper phase and in no case parent material could be reached and the examination of profile was restricted up to 8 to 10 feet. There was also no distinct zone of carbonate or 'kankar' found but lime nodules *i.e.*, small kankar were found distributed throughout the depth.

PROFILE No. 1.

Locality. Village Patan (near rest house).

District. Jabulpore.

DESCRIPTION :

0-8"	Black, clayey, cloddy, fairly dry, hard, thin roots present, lime concretions of small size, no black concretions.
8"-25"	Dark grey colour because of lime concretions, clayey, cloddy, fairly friable, very few roots present, no black concretions.
25"-38"	More greyish colour, clayey, structure not developed, fairly dry, hard, very few roots accumulations of lime concretions.
38"-67"	Brownish with black mixed, loamy, structure tending to single grain, friable, crumbles easily between fingers, very thin roots, very few lime concretions of big size.
67"-87"	The colour same as above with lighter texture, very few roots.
87"-112"	Brownish colour, silty loam, single grain structure, friable, no roots, absence of black and white concretions, fairly moist.

PROFILE No. 2.

Locality. Village Chargaon, 65 miles for Bhopal S. E., 6 miles from Buri village, 7 miles from Rini.

District. Bhopal State.

DESCRIPTION :

0"-15"	Greyish black, clayey, heavy cracks, big clods breaking into angular shape with definite laminations, dry, very thin roots present, white as well as black concretions present, but black few.
15"-39"	Moist darker than above, clayey, small clods angular 1"-2", fairly friable, breaking into small clods, shining natural cleavages, white and black concretions.
39"-75"	Mixture of brownish patches, clayey, definite laminated structure plates 1"-2" thick, fairly friable, white concretions, very few black concretions, moist.

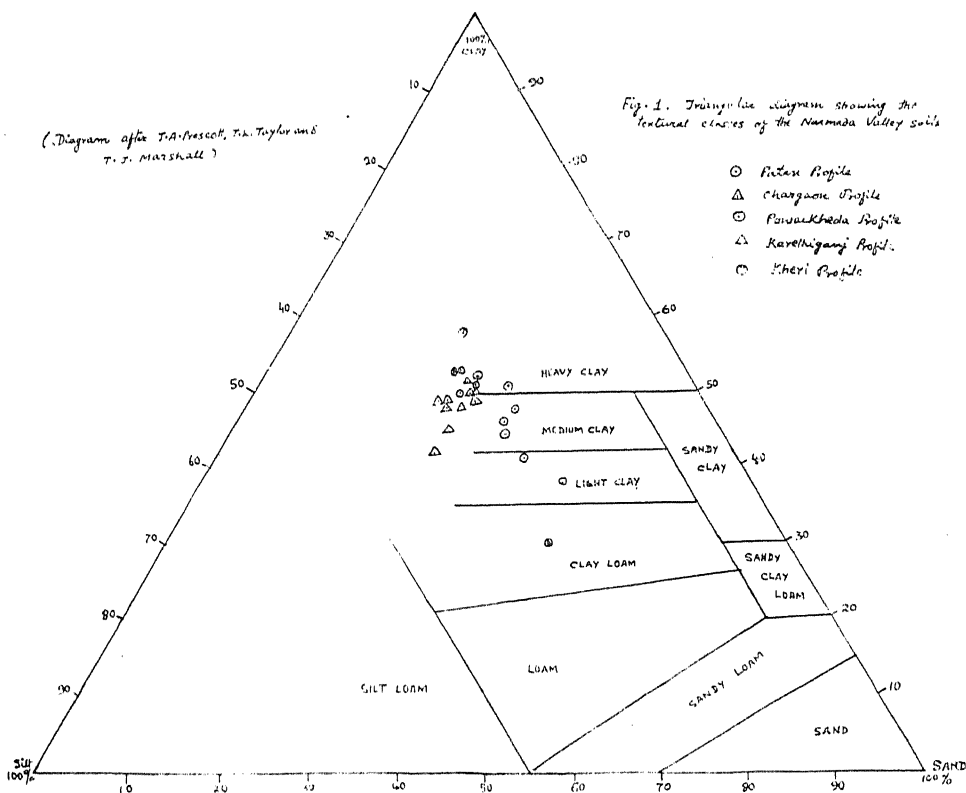
75''-96''	Definite brown colour, more brown at lower depth, clayey, structure not well developed but tendency towards laminae, moist, but friable, no roots, white concretions of bigger size.
96''-111''	Definite brown colour, moist, loamy, structure not well developed, friable, no black or white concretions.
<b>PROFILE No. 3.</b>	
Locality.	Government Experimental Farm, Powarkheda.
District.	Hoshangabad.
<b>DESCRIPTION :</b>	
0''-8''	Dark grey, clayey, cloddy, fairly dry, hard, breaking into clods, very fine thin roots present, lime concretions present, small size black concretions also present.
8''-26''	Dark grey, clayey, moist, hard, breaking into angular clods, black and white concretions present.
26''-61''	Colour darker than above, clayey, moist but not sticky, crumbling between fingers under pressure, very few roots, black concretions present, but less than the above.
61''-72''	Lighter colour, clayey, tendency of breaking into plates with natural cleavages, sticky, no roots, very few white concretions, but more of black concretions, moist.
72''-98''	Still lighter colour changing into light brown, clayey, structure not developed, very sticky, very few white concretions present, moist, very small light black mottling, small nodules.
<b>PROFILE No. 4.</b>	
Locality.	Village Karehiganj (near railway station) near village field, on the side of the railway line.
District.	Hoshangabad.
<b>DESCRIPTION :</b>	
0''-8''	Greyish black, clayey, cloddy structure, clods breaking into angular cubes with natural cleavages, hard, thin roots present, black and white concretions found in large quantities, dry.
8''-32''	Colour same as above, big clods, tendency to form columnar structure, breaking into smaller clods, between fingers, not friable, no roots, longitudinal cracks, moist.
32''-57''	Blackish grey, clayey, structure not developed, fairly sticky, presence of white and black concretions in large quantities, moist.
57''-83''	Slightly lighter colour than above, clayey, undeveloped structure, sticky, black and white concretions in lesser quantity than the above layer, fairly moist.
83''-121''	Same colour as above layer, clayey, tendency to platy structure with natural cleavages, moist, not sticky, easily breaking between fingers, fairly friable, lower part more friable, black and white concretions more white than black, size of concretions larger than in the first two horizons, moist.
<b>PROFILE No. 5.</b>	
Locality.	Kheri Farm, Jabulpore.
District.	Jabulpore.

# DESCRIPTION :

0"-12"	Hardy, clayey, fairly moist.
12"-24"	Tendency to platy structure, and tendency to break [into] angular clods.
24"-36"	Clayey texture, more moist, no definite cleavage.
36"-48"	Clayey texture, sticky, moist.
48"-60"	Clayey texture, sticky, moist.
60"-72"	Clayey texture, sticky, moist.
72"-84"	Clayey texture, sticky but tendency to break into clods, perhaps due to lime concretions, friable, moist.
84"-96"	Clayey texture, moist.

## PHYSICAL CHARACTERISTICS OF SOILS.

**TEXTURE.**—The mechanical composition of these soils show (Table 1) that these soils are clayey in texture. The clay fraction of first 3 feet in all these soils vary between 45 and 55% and when expressed in the triangle (Fig. 1) of Prescott, Taylor and Marshall (7) it shows that these soils mostly belong to heavy clay and medium clay class. In the brown horizon, which occurs at lower depth, the clay content is slightly less than the above horizon. The distribution of clay fraction is uniform throughout the depth and thus there is no illuviation or eluviation at any depth. The sand varies from 16.9 to 21.1% except in profile No. 1 where it varies from 19.7 to 43.7% and the distribution is not uniform.



The volume expansion (Table 2) is also very high and is a characteristics of black soils of India. Coutts (3) has established a similar relation between the clay content and the volume expansion. The nature of clay mineral is also directly related with this property. Montmorillonitic type of clays generally show higher volume expansion and it has been found (explained in other communication) that the clay minerals present in these soils belong to montmorillonite group. The apparent specific gravity of these soils ranges between 1.4 and 1.6 which also indicates the heavyness of these soils. Higher the finer fraction lower is the specific gravity and vice versa.

The carbonate content varies between 1.0 and 5.0% in the upper horizon, and is generally increased with the depth. The soil, therefore, has enough of lime reserve.

PORE SPACE DISTRIBUTION.—The soil aeration, specially for irrigated soil is closely related to the texture and structure of the soil as the movement of water within the soil is mostly through larger voids. Thus the non-capillary porosity is more important in characterising the structural properties, and the permeability of a soil. An ideal soil should have the pore-space with equal distribution between the larger pores and the smaller pores i.e., between non-capillary pores and capillary pores.\* Such a soil will have good aeration,

TABLE 1.  
MECHANICAL COMPOSITION OF THE SOILS.

Depth in inches.	Coarse sand%	Fine sand %	Silt %	Clay %	Carbo-nates %	Total %	Moisture %
PROFILE 1.							
(Patān)							
0"-8"	0.19	23.60	24.50	49.30	0.78	98.37	7.26
8"-25"	0.83	19.70	24.00	50.10	1.59	96.22	6.34
25"-38"	0.47	20.40	23.90	47.40	6.17	98.34	7.83
38"-67"	2.00	31.70	23.10	39.90	3.36	99.26	8.37
67"-87"	0.12	38.70	20.30	36.40	4.40	99.92	6.98
87"-112"	0.37	43.10	26.40	30.10	1.98	101.95	6.04
PROFILE 2.							
(Chargaon)							
0"-15"	2.40	18.90	27.90	47.80	2.69	99.69	6.47
15"-39"	2.20	18.20	29.90	48.10	5.44	103.84	6.71
39"-75"	1.80	20.40	26.40	45.40	5.04	99.04	6.17
75"-96"	1.00	19.70	26.90	39.40	9.98	96.98	4.79
96"-111"	0.55	20.40	30.60	37.50	10.34	99.39	5.83

\*Since the non capillary prosity is the sum of the volumes of the larger pores, which will not hold water tightly by capillarity and are normally filled with air and are responsible for the air capacity and ready percolation of water through soil, its determination and proportion to the total prosity is very essential, specially so in permeability studies. Capillary porosity on the other hand is the sum of the volumes of the small pores that hold water by capillarity and they are responsible for the water capacity of soils. However, direct determination of non-capillary porosity is not possible. Advantage is taken here of the total porosity and the moisture held at m.e. which generally is near the field capacity is converted from weight basis to the volume basis and thus the volume occupied by water is deducted from the total volume held by air alone (i.e., total porosity) which will give the volume of air left unoccupied by water. This volume of air left unoccupied gives the volume that will be occupied by non-capillary moisture.

TABLE 1. (Continued)

PROFILE 3.							
Powarkheda)							
0"-8"	8.80	20.50	23.20	44.60	1.69	98.79	5.53
8"-26"	9.90	19.80	21.10	45.60	3.72	100.12	6.19
26"-61'	9.90	19.50	23.50	42.80	3.91	100.10	6.27
61"-72"	6.50	18.70	19.50	46.80	6.54	98.04	5.89
72"-98"	4.60	17.50	21.50	47.00	4.28	94.98	5.77
PROFILE 4.							
(Karelhinganj)							
0"-8"	0.98	21.10	24.60	46.80	5.38	98.86	7.13
8"-32"	2.70	19.00	23.30	47.30	6.69	98.99	7.02
32"-57"	0.76	19.30	26.30	43.10	6.70	96.16	7.30
57"-83"	3.50	18.80	23.80	46.60	5.69	98.39	7.50
83"-121"	6.20	17.70	25.10	47.10	4.39	99.49	7.07
PROFILE 5.							
(Kheri)							
0"-12"	0.26	16.90	21.30	55.50	1.07	94.73	6.95
12"-96"	1.10	19.10	25.50	52.20	0.02	98.12	6.34

TABLE 2.

## KEEN-RACZKOWSKI DETERMINATIONS.

Depth in inches Y	Moisture holding capacity %	Real Specific Gravity %	Apparent Specific Gravity %	Volume Expansion %
PROFILE 1.				
(Patan)				
0"-8"	54.81	2.86	1.55	29.93
8"-25"	54.60	2.72	1.57	29.74
25"-38"	54.18	2.70	1.49	26.74
38"-67"	50.29	2.90	1.47	24.35
67"-87"	48.13	2.84	1.45	22.18
87"-112"	42.39	2.80	1.51	19.13
PROFILE 2.				
(Chargaon)				
0"-15"	50.66	2.80	1.59	30.49
15"-39"	52.62	2.69	1.51	29.21
39"-75"	53.35	2.61	1.47	28.80
75"-96"	47.54	2.56	1.47	21.63
96"-111"	50.63	2.61	1.43	20.18
PROFILE 3.				
(Powarkheda)				
0"-8"	45.13	2.54	1.51	22.37
8"-26"	44.72	2.54	1.54	21.67
26"-61"	43.71	2.70	1.65	25.13
61"-72"	43.71	2.70	1.65	25.13
72"-98"	44.91	2.65	1.63	27.85

TABLE 2. (Continued)

PROFILE 4.				
(Karelhiganj)				
0"-8"	53.84	2.39	1.48	24.53
8"-32"	54.46	2.27	1.45	27.87
32"-57"	55.46	2.58	1.44	25.23
57"-83"	58.73	2.61	1.41	27.96
83"-121"	54.11	2.54	1.51	33.91
PROFILE 5.				
(Kheri)				
0"-12"	54.46	2.69	1.52	31.47
12"-96"	53.70	2.67	1.54	26.84

free drainage and good water holding capacity. Total porosity in all these soils varies between 52 and 58% (Table 3) but these soils, however, do not show an ideal condition in which the distribution between non-capillary porosity and capillary porosity should be equal. The percentage of non-capillary porosity over the total porosity in these soils varies from 22 to 48% in the surface soil. Considering the heavy nature of these soils containing about 45% clay in the surface soil, it can be said that the percentage distribution of non-capillary and capillary pores is fairly good, specially in profile 3 and 5 where the values of non-capillary porosity over total porosity are 42.1 and 48.5% respectively. The reason is that these profiles were taken from cultivated fields of Powarkheda Farm (Hoshangabad) and Kheri Farm (Jubbulpore) whereas profiles 1, 2 and 4 were from virgin land. However, the total porosity in all these profiles, whether from cultivated or virgin land, is practically the same, but in cultivated soil non-capillary porosity is higher than virgin soil but shows practically the same percentage of non-capillary porosity in the lower horizons, which is not cultivated.

The importance of non-capillary porosity in drainage problem and structural properties is obvious. The ability of soils to drain naturally as well as their need for artificial drainage are correlated with non-capillary porosity or with its air capacity. Kopecky<sup>5</sup> claims that soils that do not have air-capacity of 10% or greater, are in need of artificial drainage. These soils, however, have much higher values than 10% and do not indicate the necessity of artificial drainage in near future, provided the structure is not destroyed.

**MOISTURE RELATIONSHIP.**—Water holding capacity of these soils is very high (Table 2) and varies between 43.5 and 58.7%. The hygroscopic coefficient is associated with colloidal content of soil and also indicates moisture available at tension nearly 31.6 atmosphere percentage which for all practical purposes is unavailable to plant. The content of hygroscopic moisture is, however, fairly high in these soils. Moisture equivalent, according to Veihmeyer and Hendrickson<sup>14</sup> is a good measure of field capacity in laboratory test and has been widely used as a measurement for characterising the moisture retention of soils. Moisture equivalent of these soils varies from 27.0 to 36.3% and is characteristic of heavy soils.

The permanent wilting percentage has been defined by Veihmeyer and Hendrickson<sup>13</sup> as the lower limit of available soil moisture and can be obtained by field or laboratory method. The permanent wilting percentage

TABLE 3.

TOTAL POROSITY AND NON-CAPILLARY POROSITY.

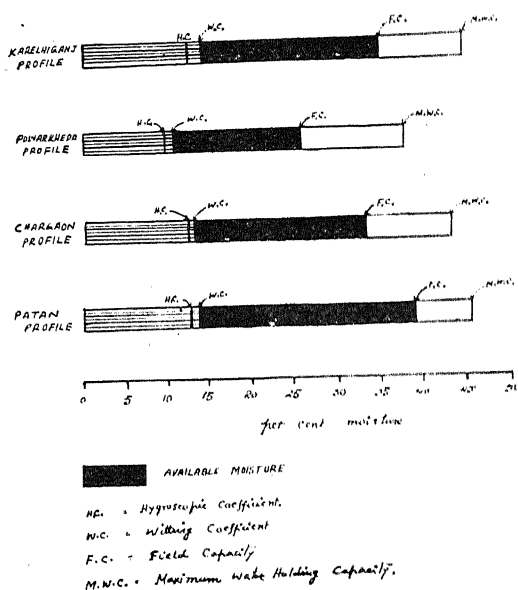
Depth in inches.	Total porosity % by volume	Non-capillary porosity % by volume	%non-capillary porosity over total porosity
PROFILE 1.			
0"-8"	58.82	12.91	21.96
8"-25"	56.16	10.56	18.81
25"-38"	57.99	18.16	31.30
38"-67"	52.19	...	...
67"-87"	50.27	...	...
87"-112"	48.87	...	...
PROFILE 2.			
0"-15"	58.34	16.89	28.94
15"-39"	56.93	20.22	35.53
39"-75"	57.36	21.41	37.33
75"-96"	52.74	19.18	36.38
96"-111"	54.58	23.99	43.95
PROFILE 3.			
0"-8"	52.47	22.11	42.14
8"-26"	51.66	18.57	35.93
26"-61"	51.40	18.17	35.54
61"-72"	51.69	19.93	38.56
72"-98"	52.66	20.13	38.22
PROFILE 4.			
0"-8"	54.76	17.87	32.64
8"-32"	55.68	17.58	31.58
32"-57"	56.07	21.14	37.71
57"-83"	58.41	25.02	42.84
83"-121"	53.31	23.12	43.36
PROFILE 5.			
0"-12"	58.06	28.19	48.56
12"-96"	55.05	29.99	54.04

or wilting coefficient was determined in laboratory by growing wheat seeds in small pots and after sufficient growth, the plants were allowed to wilt and percentage of moisture at which they permanently wilted were determined. The soils 1, 2 and 4 have nearly the same value (Table 4) which varies between 16.1 and 16.8% whereas soil No. 3 has only 13.0%. The determination of wilting percentage together with that field capacity gives the total amount of water that can be held in available form by a soil. Fig. 2 shows the range of available moisture of these soils. The soil from Powarkhedda contains 16.7% available



moisture. Chargaon soil shows 23.5%, Kareliganj 25.2% and Patan soil 30.5% available moisture.

Fig. 2. Showing Available moisture in Narmada Valley Soils.



It has been found that wilting point value is fairly definite lower limit of available water to the plant and in many cases is taken as the moisture at 15 atmosphere percentage. Similarly, Richard and Weaver<sup>8</sup> have shown that 1/3 atmosphere percentage corresponds approximately to the moisture equivalent while Hygroscopic coefficient at 3.3%  $H_2SO_4$  corresponds to nearly 31.6 atmosphere percentage. The figures obtained in this study at different soil moisture equilibrium points, help to establish a certain relation among the 15 atmosphere percentage, 1/3 atmosphere percentage, 31.6 atmosphere percentage and the saturation percentage of these soils. It shows that the saturation percentage is approximately 1.6 times the 1/3 atmosphere percentage *i.e.*, field capacity and 3 times the 15 atmosphere percentage *i.e.*, wilting point and nearly the same times as that of hygroscopic moisture (Table 4). It is, therefore, indicative that not only the moisture retaining capacity of these soils is high but the moisture releasing capacity is equally high, which can be judged from the difference between the moisture held at wilting point and the moisture held at hygroscopic moisture. The difference between these two limits is only 1.0%.

**STRUCTURAL PROPERTY.**—Soil structure is generally regarded as being an important factor in irrigation agriculture. Since the structure is directly responsible for the arrangement and cohesion of the primary soil particles, the other

related properties such as porosity, permeability, the state of aggregation and dispersion of the soil are largely dependant upon the stability of the soil structure.

Porosity has already been dealt with earlier and permeability will be discussed after the state of aggregation. Out of many methods of expressing the structural capacity of a soil, a much better and quick index is provided by the analysis of water stable aggregates of the soil. Such an analysis measures the relative distribution of the various size of aggregates and permit a calculation of the percentage aggregates of the finer mechanical separates into large compound particles, indicating thereby the capacity of primary particles namely sand, silt and clay to be aggregated under natural condition. The distribution of size particles and the capacity of silt and clay to form aggregates are essential to furnish a complete picture of the structural capacity of the soil. Similarly the analysis of water-stable aggregates provides the information of the non-dispersibility of soil under irrigation.

TABLE 4.

COMPARISON OF MOISTURE RETENTION VALUES FOR SOILS AND THEIR RATIOS.

Depth in inches.	Hygroscopic coefficient at 3.3% $H_2SO_4$ or 31.6 atmos- phere percen- tage.	Wilting coefficient or 15 atmosphere percentage.	Moisture equivalent or 1/3 atmos- phere percen- tage.	Maximum water holding capacity or Saturation percentage.
PROFILE 1.				
0"—8"	15.48	16.37	35.55	54.81
8"—25"	14.33		36.30	54.60
Ratios	1.05		2.1	—
	3.5	3.3	1.7	—
PROFILE 2.				
0"—15"	15.09	16.14	30.30	50.66
15"—39"	15.52		31.55	52.62
Ratios	1.05		1.9	—
	3.3	3.1	1.6	—
PROFILE 3.				
0"—8"	11.37	13.00	28.45	45.13
8"—26"	12.28		27.35	44.72
Ratios	1.2		2.2	—
	4.06	3.4	1.6	—
PROFILE 4.				
0"—8"	14.09	16.88	31.70	53.84
8"—32"	14.93		32.90	54.46
Ratios	1.2		1.8	—
	3.8	3.1	1.7	—
PROFILE 5.				
0"—12"	15.61	—	35.10	54.46
Ratios		3.1	1.6	—

The aggregate analysis was carried according to Russell and Tamhane<sup>9</sup> where the standard sieves with opening of 1.5 mm., 1.0 mm., 0.5 mm., 0.2 mm., and 0.1 mm., were used with simple dispersion according to Puri<sup>8</sup>. The lowest limit of particles was taken as 0.02 mm.

TABLE 5.

AGGREGATE ANALYSIS OF THE SOILS.

Size of particles mm.	Profile 1 8"-25"		Profile 2 6"-15"		Profile 2 15"-39"		Profile 3 6"-8"		Profile 3 8"-26"		Profile 4 8"-32"	
	A.A.*	U.D.*	A.A.	U.D.	A.A.	U.D.	A.A.	U.D.	A.A.	U.D.	A.A.	U.D.
1.5	6.37	...	2.11	...	1.60	...	2.11	...	4.80	...	1.44	...
1.5-1.0	9.46	...	2.11	...	2.13	...	2.11	...	4.84	...	2.46	...
1.0-0.5	33.22	...	14.77	...	18.67	...	16.25	...	23.67	...	18.62	...
0.5-0.2	17.91	...	32.07	...	28.65	...	29.12	...	30.47	...	37.12	...
0.2-0.1	5.79	...	24.26	...	11.47	...	31.96	...	12.25	...	8.02	...
0.1-0.02	25.86	...	24.45	...	37.21	...	18.01	...	23.20	...	31.43	...
2.0-0.2	...	0.83	...	2.40	...	2.20	...	8.80	...	9.90	...	2.70
0.2-0.02	...	19.70	...	18.90	...	18.20	...	20.50	...	19.80	...	19.00
0.02-0.002	0.39	24.90	0.24	27.90	0.28	29.90	0.38	23.20	0.20	21.10	0.31	23.30
0.002	0.07	50.10	0.07	47.80	0.06	48.10	0.06	44.60	0.08	45.60	0.06	47.30

\* A.A.—Aggregate Analysis. U.D.—Ultimate Dispersion.

Tiulin<sup>12</sup> has suggested that only aggregates 0.25 mm. are responsible for favourable structural relationship. Bayer and Rhodes<sup>2</sup> took the limit of the size of aggregates from size frequency distribution curves of the soil, determined with and without dispersion. The diameter of the particles corresponding to the point of intersection *i.e.* 0.05 mm. on the curve was taken as the lower limit of the size of aggregates which were responsible for the structural relationship of the soil. However, there is no fixed limit, so far advanced to be considered as the lowest limit of the crumb.

TABLE 6.

THE STRUCTURE CAPACITY OR EXTENT OF AGGREGATION OF THE SOILS.

Profile	Depth inches	Mechanical separates larger than 0.02 m.m. per cent.	State of Aggregation Aggregates larger than 0.02 m. m. per cent.	Degree of Aggregation
				Mechanical separates smaller than 0.02 m. m. aggregated into units larger than 0.02 m. m. per cent.
Profile 1	8"-15"	22.12	72.68	93.32
Profile 2	0"-15"	23.99	73.01	96.04
	15"-39"	25.84	70.16	92.12
Profile 3	0"-8"	30.99	64.61	93.62
	8"-26"	33.42	63.78	95.78
Profile 4	8"-32"	28.39	67.31	94.00

In the present study, the limit of 0.02 mm. was used as the lower limit of aggregation on the basis that the particles below the limit of 0.02 mm. as obtained in simple water dispersion are only about 4.0% in these black soils. Middleton<sup>6</sup> has employed the limit 0.05 mm. for his dispersion ratio. It can thus be seen from the distribution of aggregation (Table 5) that nearly 85.0 to 95.0% aggregation in these soils to a depth of about 2 to 3 feet have their aggregates between 1.0 mm. and 0.02 mm. It further shows that mechanical separates below the limit of 0.02 mm. are aggregated into units larger than 0.2 mm. to the extent of 96.04%. A very interesting point regarding these black soils, is that the particles 0.02 mm. size are only about 4% in the aggregate analysis whereas in the mechanical analysis the percentage of these particles varies between 67.0 and 78.0%. This shows that nearly all the silt and clay is completely aggregated in these soils. The degree of aggregation (Table 6) as calculated according to Baver and Rhodes<sup>2</sup> show that it is between 93.32 and 96.04% indicating thereby a good capacity of maintaining the soil tilth under irrigation. The dispersion ratio of these soils which gives the proportion silt + clay likely to slake away is very low (Table 7). This finding suggests that the stability of the structure in these soils is very good and is not likely to get easily dispersed under irrigation.

TABLE 7.

PERCENTAGE OF SILT AND CLAY AS OBTAINED IN SIMPLE WATER DISPERSION AND ALSO IN MECHANICAL ANALYSIS.

Depth in inches	% Clay plus Silt M. A.	% Clay plus Silt water dispersion	Dispersion ratio.
PROFILE 1.			
0"-8"	73.80	4.70	6.3
8"-25"	74.10	5.20	7.0
25"-38"	68.30	5.20	7.7
PROFILE 2.			
0"-15"	75.70	3.00	4.0
15"-39"	78.00	3.40	4.3
39"-75"	71.80	4.20	5.9
PROFILE 3.			
0"-8"	67.80	4.40	6.6
8"-26"	67.70	2.80	4.8
26"-61"	66.70	3.90	5.9
PROFILE 4.			
0"-8"	66.40	3.80	5.7
8"-32"	70.60	4.30	6.1
32"-57"	69.40	4.10	5.9

#### PERMEABILITY

Information on the rate at which water enters and moves through the soil is useful not only in connection with the changes likely to be brought about during

percolation of water through the column of soil but it also provides the information about the structural stability of the soil.

In the absence of field study of permeability because of the expense and restrictions encountered with field work, an approximate estimate of the comparative rate of percolation of these soils are studied in the laboratory as suggested by Slater and Byer<sup>10</sup>. Permeability as measured in the laboratory is related to many factors ; such as dispersion ratio, structural stability and base status of soils. In view of this finding the rate of percolation of these soils under constant laboratory conditions was studied and compared with other physical properties.

Permeameter used in the present study consists of six cylinders of uniform cross-section and a constant head of water was maintained. The rate of percolation was measured at fixed intervals, using formula  $P = \frac{QL}{TAH}$ . From the values it is evident that in the first 12 hours the permeability decreases gradually and afterwards it becomes more or less constant. (Table 8).

TABLE 8.  
RATE OF PERCOLATION IN CENTIMETERS UNDER A CONSTANT HEAD OF  
9 C. M. OF WATER.

Time		Profile 1 (Patan) 0"-25"	Profile 2 (Chargaon) 0"-39"	Profile 3 (Powarkheda) 0"-26"	Profile 4 (Kurelhiganj) 0"-32"
1st	Hour	1.28	7.18	8.25	5.82
2nd	"	1.23	6.74	7.97	5.40
3rd	"	1.15	6.54	7.97	5.32
7th	"	0.94	5.79	7.03	4.72
12th	"	0.86	5.64	6.64	4.24
24th	"	0.75	5.63	6.65	4.35
Average of 24 hours.		0.90	5.87	7.32	4.60

The relative permeability of Powarkheda soil is 7.32 cm/hour. Chargaon soil has 5.87 cm/hour while Patan soils is very low in permeability. Powarkheda soils apparently show a better rate of percolation and the least one is Patan soil. Bayer<sup>11</sup> has shown that there exists a direct relationship between the non-capillary porosity and the soil permeability. In the present case, Powarkheda soil which has a better rate of percolation has 22.0% non-capillary porosity whereas Patan soil which has a low rate of percolation has only 12.9% of non-capillary. Thus there is a good relation between non-capillary porosity and the permeability. However, the degree of aggregation does not exhibit any such difference between these soils. Thus laboratory study of permeability, porosity, and structural analysis help to diagnose the behaviour of different soils under field irrigation.

**SALT CONTENT, EXCHANGEABLE SODIUM AND SOIL REACTION.**—In as much as the physical properties are a good guide to judge the irrigability of soils, the content of soluble salt, percentage saturation of sodium in the exchange complex and pH are also helpful in determining the suitability of soils for irrigation. The total soluble salt in these soils is below 0.15% which is quite

low and the pH is between 7.8 and 7.9. Similarly exchangeable sodium in these soils is practically negligible (Table 9). Thus the soils do not show any tendency of developing them into saline soils under irrigation.

TABLE 9.

T. S. S., pH AND EXCHANGEABLE SODIUM

	Profile No. 1		Profile No. 2		Profile No. 3		Profile No. 4.	
Depth	0"-8"	8"-25"	0"-15"	15"-39"	0"-8"	8"-26"	0"-8"	8"-26"
T. S. S.	0.12	0.13	0.116	0.112	0.053	0.08	0.16	0.17
pH	7.85	7.9	7.91	7.83	7.8	7.9	7.89	...
Exchangeable Sodium m.e/ gm. 100 soil	0.09	0.10	traces	traces	nil	nil	0.12	0.2
% saturation with sodium.	Since exchangeable sodium is negligible sodium saturation is not calculated.							

DISCUSSION.—In considering the suitability of a soil for irrigation agriculture, the texture and structure are important factors which govern the movement of water through the soil. In a coarse texture soil water will have free movement and will rapidly go down as the rate of percolation will be higher whereas the clayey soil much will depend upon the structure and porosity of the soil and will have a slow rate of percolation but will have high water holding power. Under irrigation, depth of soil and water holding capacity are equally important. All these soils are deep and clayey in texture with high water holding and high water releasing capacity and does not indicate necessity of frequent irrigation. More frequent irrigation, as required for shallow soils and having low water holding capacity necessary results in increase cost in water, labour and increase cost of production. These soils have a wide range of available moisture which suggests that the plant growth in these soils will not be adversely affected even if the interval between two consecutive irrigations be kept at longer intervals, than is usually done in light textured soils. Naturally the climatic factors and the crops grown will play a great part in the assumption but in comparison with light textured soils under same climatic conditions these soils will not effect the plant growth so badly. Not only the moisture retaining capacity of these soils is high but moisture releasing capacity is also equally high as can be judged from the difference between moisture at 15 atmosphere percentage and 31.0 atmosphere percentage *i.e.*, between wilting point and the hygroscopic moisture which is only 1.0%. Similarly the total porosity in these soils is nearly 55% and the distribution of the total porosity between non-capillary porosity and capillary porosity is of the order 35 and 65% respectively, but in case of Powarkheda *i.e.*, profile 3, the proportion of the non-capillary to capillary porosity is nearly 42.0 and 58.0% and in Khedi soil *i.e.*, profile 5 it is 48.0 and 52.0% which indicates that soils are not likely to be in need of immediate artificial drainage. Similarly the non-capillary study of all the horizons in these soils do not indicate the presence of any impermeable layer throughout the depth examined. Under these conditions, it is not likely that these soils would either get water logged or would develop salinity or alkalinity as the content of soluble salts and the percentage saturation of sodium in exchange complex is insignificant. The aggregate analysis which furnishes the water stability of the natural structure and the capacity of silt and clay to form aggregate shows that nearly all the clay and silt fraction in these soils is aggregated into particles greater than 0.02 mm. and the degree of

aggregation is between 93.32 and 96.04 indicating thereby the capacity of soil to maintain good tilth. The dispersion coefficient of these soils, which is an index of the ease with which soil particles slake in water, is only about 5.0 which is very low. In testing soil permeability many factors which are not yet fully understood and correlated influence the rate of percolation but when a percolation rate is considered along with other related physical determinations, it gives a useful information. From all the factors consider above it may be said that irrigation of these black soils is possible without any probable danger of either development of salinity or water-logging condition but considering the clayey texture of these soils irrigation should not be applied indiscriminately and should be controlled to suit the need of crops with adequate facilities of drainage.<sup>11</sup>

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# IONIC DIFFUSION IN SOIL

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## I. INTRODUCTION

A technique for the measurement of diffusion coefficients of anions and cations separately under a known total ionic concentration was reported in an earlier communication.<sup>1</sup> Using that technique the effective fractional areas of water channels in beds of porous media, more or less resembling soil, were measured. In those experiments the pore-space was completely filled with the liquid. In actual field conditions, however, except under water-logged soils, the soil pore-space contains partly liquid and partly air. The technique has therefore been suitably modified, in the present investigation as to measure the quantity of ion diffused in soils. As ionic diffusion depends on the sizes of the pores filled up and the water channels present in the pore-space, measurements were made under different values of suction applied to the soil and the results obtained are discussed in relation to the movement of salts in the soil pore-space.

## II. EXPERIMENTAL

Buchner funnels of two different diameters were used as diffusion vessels. Funnels of the same diameter were ground at the top such that they closely touch each other on the rim when pressed together. To attain field conditions of packing, as far as possible in the laboratory, Woburn soil was used in the present investigation. It is a sandy soil and the results of mechanical analysis show that the soil contains 7.2% clay, 15.1% silt, 14.8% fine sand and 62% coarse sand. The dried and weighed funnels were filled with the soil and connected to a filter pump with a mercur manometer in series. Circular rubber bands were fitted so as to project beyond the rims of the funnels the better to retain the soil. They also served as containers for the liquid which was made to percolate through the soil. N/10 KBr solution was percolated through one funnel while N/10,  $\text{NH}_4\text{NO}_3$  solution was percolated through the other. The soil was washed thoroughly with the electrolytes in a constant temperature room at 20.5°C for about 6 hours when it would pack itself uniformly up to the top of the funnel and attain a uniform suction pressure. The rubber bands round the rims were slipped out and the excess of soil over the ground rim was carefully removed. It was convenient to allow the soil to project a little over the ground surface so that when the two funnels were pressed together a better contact could be established between the soils. The funnels were weighed and then joined rim to rim together. A metal collar was slipped over the funnels and tightly screwed to keep them together. They were kept horizontally as to have no preferential gravity movement of the liquids in the direction of diffusion. The open ends of the funnels were sealed with soft wax as to avoid evaporation. All the experiments were carried out only for 24 hours as the depths of the funnels were between 2.5 and 3.0 cm.



After a known time of diffusion the collar was removed and the funnels were carefully separated. They were weighed again and slight difference in weight, if any, was noted for making the necessary corrections. The soil was then dried up in the funnels for 24 hours at 105°C and the loss of weight was noted. The soil in the funnel containing  $\text{NH}_4\text{NO}_3$  was washed carefully with distilled water and the wash was collected to estimate the bromide ion diffused. Usually the wash so obtained was slightly coloured with the organic matter present in the soil and it was decolorised by boiling with hydrogen peroxide before estimating the bromide ion volumetrically.

### III. RESULTS

If two solutions containing ions of equal mobilities but chemically distinguishable and of the same concentration  $C_0$  are brought into contact at a plane surface, the amount,  $q$ , of the ions that diffuses across area  $A$  of this plane in time  $T$  is related to the diffusion coefficient  $D$  by the equation

$$D = \left( \frac{2q}{C_0 A} \right)^2 \frac{\pi}{4T} \quad \dots \quad (1)$$

If the solutions were held in porous beds, say of the same porosity, the quantity of the ion diffused in a given time depends on the effective fractional area of the cross section,  $f$ , given by the equation

$$D = \left( \frac{2q}{C_0 A f} \right)^2 \frac{\pi}{4T} \quad \dots \quad (2)$$

The value of  $f$  depends upon the twists and constrictions obstructing free diffusion. If  $q$ ,  $A$  and  $T$  are measured, knowing the value of  $D$  the value of  $f$  can be calculated. The results obtained from the diffusion measurements are given in the table below. The value of  $D$  at 20.5°C for the bromide ion was taken as 1.78  $\text{cm}^2/\text{day}$ .

EFFECTIVE FRACTIONAL AREAS CALCULATED FROM DIFFUSION MEASUREMENTS  
IN WOBURN SOIL.

$T$ in days	Suction pressure cm. Hg	$A$ $\text{cm}^2$	Porosity of air P (air)	Porosity of liq. P (liq.)	$q/C_0$ for bromide	$f_{\text{Br}^-}$	$f_{\text{Br}^-}$ P (liq.)
1.0	25.1	33.03	0.293	0.174	0.37	0.015	0.085
1.0	25.1	17.69	0.212	0.179	0.26	0.020	0.109
1.0	13.5	33.03	0.298	0.174	0.99	0.040	0.223
1.0	7.5	33.03	0.224	0.244	1.76	0.071	0.294
1.0	7.5	17.69	0.223	0.238	0.71	0.054	0.225

In this technique there is possibility of anionic exchange and of equilibrium between the ions and the clay particles, which, however, is not likely to affect significantly the conclusions.

The funnels used in the experiments slightly differed in their areas of cross section and their mean values were taken. In spite of the uniform suction applied, the values of porosity (both P (air) and P (liq.)) differed slightly from one funnel to the other and in this case also the mean values were taken.

### IV. DISCUSSION

Migration of ions up to the plant roots takes place (a) by the viscous movement of the soil solution through the pore-space and (b) by ionic diffusion. As long as there is drainage, viscous flow is possible. But when once the drainage

stops ionic diffusion alone helps ionic migration. In the three phase system of the soil, the air and the solid material can be assumed to act together in forming the twists and constrictions in the water channels.

In the case of porous beds the ratio  $f/P$  is an index of the twists and constrictions in the water channels. The ratio calculated from the results obtained seems to depend on the suction applied and is found to vary from 0.294 to 0.085 with change in suction values from 7.5 cm. to 25.1 cm. This is due to the fact that as the suction is applied all the bigger passages where the movement of the liquid as well as the migration of ions can more easily take place, will be first exhausted and the pore-space that remains filled up will contain more twists and constrictions thus impeding the migration of the ions. This hindrance is found to increase with increase in suction applied. In other words the bigger pores that are emptied in the beginning reduce effectively the ionic migration but do not proportionately seem to reduce the total pore-space filled up by the liquid.

At a suction of 7.5 cm. applied, bromide ion contained in 1.763 c. c. of liquid diffused in one day. For the same quantity of ion to diffuse at suction values of 13.5 cm. and 25.1 cm., the periods required work out to be about 3 days and 23 days respectively. This rapid decrease in the amount of ion diffused with increase in the suction applied, is important for understanding the movement of salts in soils.

The diffusion measurements thus indicate that at high values of the suction applied the migration of ions due to diffusion is practically negligible. On the other hand a study of the flow of the liquids through narrow tubes showed that a Poiseuille flow coupled with diffusion is very effective for the movement of salts while a poiseuille flow alone was not so effective<sup>2</sup>. This explains the classical experiments of Laws, Gilbert and Warington,<sup>3</sup> where the drainage liquid after rain fall was poor in salt contents at first while the last traces were richer in salt contents. In the beginning the water passes through comparatively big channels and carries with it little salt while the last traces drain through the fine pores of the soil where the diffusion is effective and carry the diffusable salts with them.

#### V. SUMMARY

A technique for the measurement of ionic diffusion in soils was described. Knowing the diffusion coefficient of bromide ion the effective fraction areas of water channels in a sandy soil were measured under three different values of suction applied. The migration of ions was found to be greatly impeded at higher values of suction applied. The results are discussed in relation to the movement of salts and salt content of the drainage waters.

The above work was carried out at the Rothamsted Experimental Station and the author desires to record his grateful thanks to Dr. R. K. Schofield, Head of the Soil Physics Department, for his helpful suggestions and discussions during the course of the investigation. The author is also grateful to Dr. S. P. Raychaudhuri, Head of the Division of Soil Science and Agricultural Chemistry, Indian Agricultural Research Institute, New Delhi for his helpful discussions.

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# pF—WATER RELATION IN HEATED SOILS

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## INTRODUCTION

It has been shown in an earlier paper (6, 7, 8) that the permeability for water of a soil increases as the soil is heated to high temperatures. The reason for this increase in permeability has been suggested to be the increase in non-capillary pore volume brought about by the aggregation of soil particles. It has also been shown subsequently that the non-capillary pore volume increases on heating the soil by actually measuring the capillary and total pore volumes.<sup>3</sup>

The porous structure of a soil is essentially dependent upon the size of the soil particles and the mode of compaction. As the soil particles aggregate, the capillary, non-capillary and total pore volumes vary. Bayer<sup>1</sup> has studied the pF-water relation in a large number of soils and has drawn certain important conclusions. The object of the present investigation is to study the pF-water relation in the heated soils in comparison with that of normal soil. The interesting results obtained have been presented in this paper.

## EXPERIMENTAL

**THE SOIL :** The Gangetic alluvial soil of Delhi used in the earlier investigation<sup>7</sup> was employed in the present work.

**HEATING THE SOIL :** As in the previous work<sup>7</sup>, the soil was heated for 3<sup>1</sup> hours at the following temperatures, 60°C, 150°C, 225°C, 360°C, 600°C, 650°C, 800°C and 1000°C.

**TENSIOMETER TECHNIQUE :** The tensiometer technique described by Richards in his review article on the methods of measuring soil moisture tension<sup>2</sup> was employed. The experimental arrangement of the tensiometer is shown in Fig. 1.

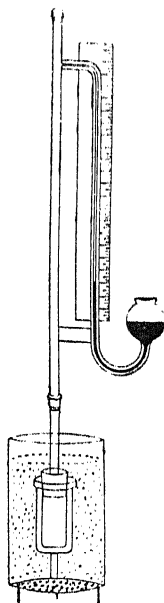


Fig. 1  
Tensiometer

A porous porcelain cylinder fitted with the tensiometer tube was supported on an iron rod (1 inch length) rivetted to be perforated bottom of a metallic can. With the iron rod support the tensiometer could be placed in a stable position, otherwise the porcelain cylinder would be subjected to strain if merely clamped. As a result of this, the rubber cork joint would yield and abrupt changes in tensiometer reading were often noticed.

A modification in the apparatus was effected by introducing a ground glass joint between the porous porcelain cylinder and the tensiometer tube. The object of this joint was to facilitate compaction of the loose soil while having the porcelain cylinder supported over the iron rod inside the soil. After the compaction was over the tensiometer tube was attached and the tensiometer was brought into action by filling it with water. Without this joint the insertion of the tensiometer into the compacted soil would disturb the state of compaction. Before the porcelain cylinder was introduced into the soil the air inside the pores was replaced by water. The cylinder filled with water was inserted into the soil. The soil was compacted by dropping the can ten times from a height of one inch. The tensiometer tube was attached. The soil was next saturated with water by passing water through the soil from above for about 20 hours in order to remove the entrapped air from the soil by solvent action. Permeability measurements (6, 7, 8) have shown that the removal of entrapped air from soil is normally complete by about 24 hours.

The zero reading of the tensiometer was taken by adjusting the water table to the centre of the porcelain cylinder. After taking the zero reading, the water table was removed. The drainable water was allowed to drain off through the perforated bottom. Two days after the removal of the water table the first tension reading was taken and at the same time a sample of the soil was removed for determining the water content. The soil water was determined by the method of oven-drying. For nearly six hours before taking the tension reading and removal of the soil sample, the can was covered to check evaporation in order to avoid non-uniformity in water distribution in the entire soil bulk. The soil was next kept open for a day to facilitate the removal of water by evaporation and again covered for about six hours before the next reading was taken. The measurements were continued in this way. Each experiment lasted over three to four weeks. Collection of air bubbles was noticeable only after a tension of 30-40 cms of mercury was reached. Nearly 15-20 points were obtained in each experiment and only some of them are shown in the graphs. Duplicate experiments were carried out in a few cases to ensure reproducibility of the results.

According to Richards if the diameter of the mercury reservoir bulb is more than 10 times the diameter of the mercury column in the tensiometer the fluctuation in the level of mercury in the reservoir is negligible. In the tensiometer used in this work the diameter of the mercury reservoir bulb was 40 times the diameter of the capillary.

**DETERMINATION OF SOIL WATER AT ZERO TENSION :** For determining the soil water at zero tension, the method of oven drying of a sample of the soil taken from the surface while keeping the water level at the surface of the soil in the can was consistently giving higher and unsteady values. Therefore an alternative procedure was adopted. It consisted in employing a glass cylinder with a side tube at the bottom, Fig. 2. A column (same as the soil column in the tensiometer experiments) of known weight of soil was taken over a perforated metallic disc with a filter paper and compacted. Water was allowed to pass through the

soil column for about twenty hours in the same way as in the tensiometer experiment. The water table was kept at the surface of the soil by adjusting the side tube and apparatus weighed. The weight of the glass cylinder without the soil and with water level at the porous disc was also determined. The weight of the cylinder with and without soil column being known the percentage of water in soil at zero tension was calculated. The accuracy of this measurement was  $\pm 0.5\%$ .

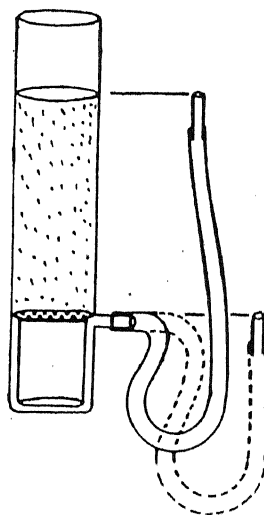


Fig. 2  
Apparatus for measuring water in soil at zero tension.

From these experiments the  $pF$ -water relations were obtained for normal and heated soils and have been shown in Figure 3.

**DETERMINATION OF INFLEXION POINT :** The inflexion point in the  $pF$ -water curve is the point at which the rate of rate of change is zero. This was determined by adopting the numerical method from a large size  $pF$ -water curve. In cases in which the inflexion was an interval instead of a point, the centre of the interval was taken as the inflexion point. An accuracy of  $\pm 0.5\%$  was obtained with difficulty. The inflexion points in the  $pF$ -water curves of normal and heated soils have been indicated in Fig. 3.

**APPARENT DENSITY :** In order to calculate the weight of water contained in 100 c.c. of the compacted soil, the apparent densities were necessary and these were taken from the previous paper.<sup>3</sup> The state of compaction in the tensiometer studies, is kept the same as in the experiments on density determinations.

**PERMEABILITY COEFFICIENTS :** The permeability coefficients which have been employed in the present paper were taken from the previous publication (6, 7, 8). These are permeabilities on the seventh day after the soil is kept submerged in flowing water.

## DISCUSSION

**THE CHARACTERISTICS AND SIGNIFICANCE OF THE  $pF$ -WATER CURVES :** Baver<sup>1</sup> has made a detailed study of the characteristics and significance of the  $pF$ -water curves of a large number of different types of soils and has arrived at certain important generalizations. According to Baver, the  $pF$  of inflexion point and the amount of water withdrawn from the soil from zero tension to the inflexion point

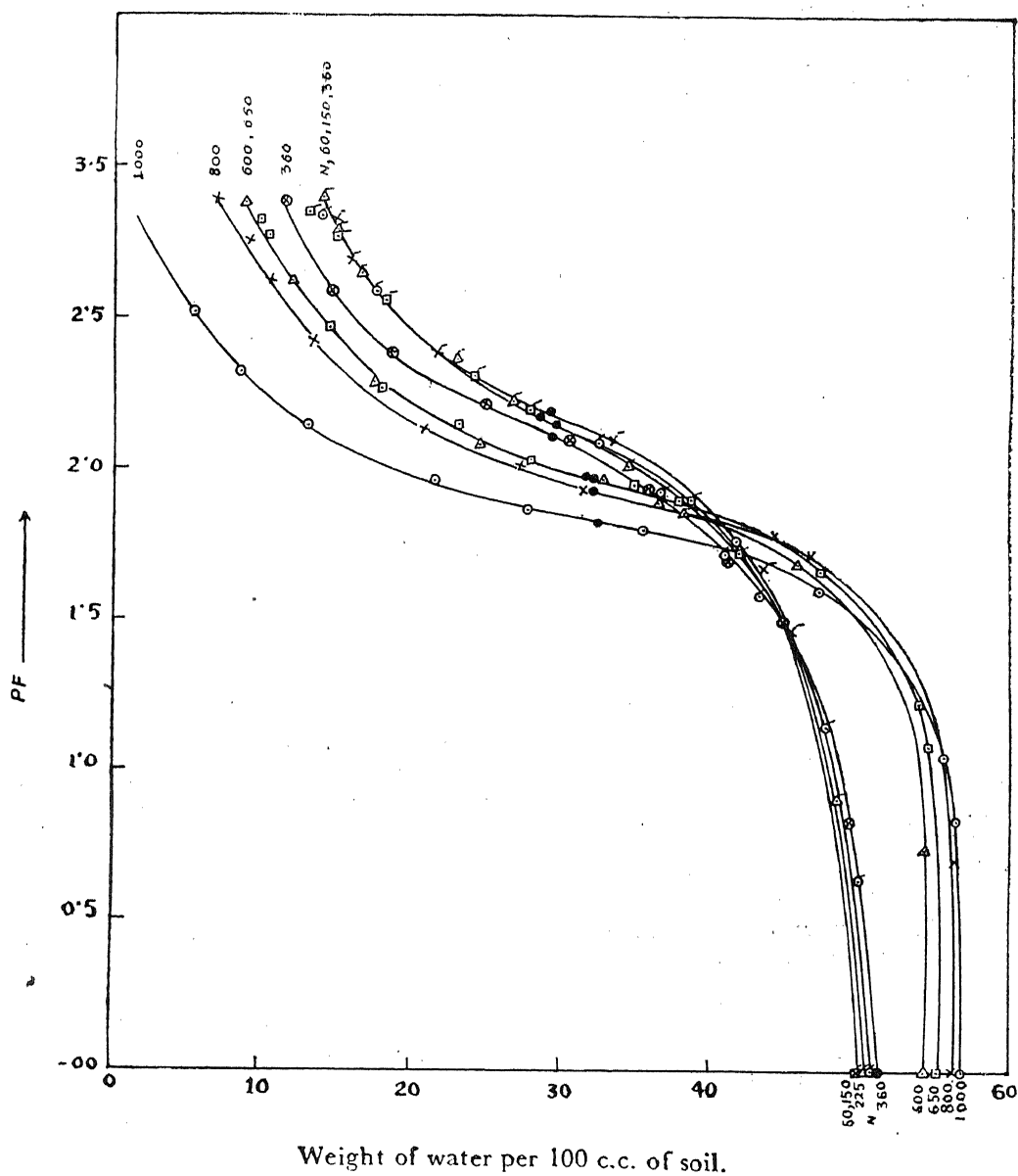


Fig. 3. pF-water relation in normal soil ( $\bar{\odot}$ ) and soil heated to 60°C ( $\bar{\times}$ ), 150°C ( $\bar{\square}$ ), 225°C ( $\bar{\triangle}$ ), 360°C ( $\bar{\otimes}$ ), 600°C ( $\bar{\Delta}$ ), 650°C ( $\bar{\square}$ ), 800°C ( $\bar{\times}$ ), 1000°C ( $\bar{\odot}$ ) with inflexion points ( $\bullet$ ).

are significant factors and are related to permeability. The permeability increases as the amount of water withdrawn from zero tension to inflexion point increases and it also increases as the pF of inflexion point decreases. In the light of these generalizations, the changes in the pF-water curves of normal and heated soils are studied and are shown in Table I and Fig. 4.

TABLE I

Temperature to which soil is heated	Weight of water per 100 c.c. of soil at zero tension V <sub>z</sub>	Weight of water per 100 c.c. of soil at inflexion point V <sub>x</sub>	pF of inflexion point pF <sub>x</sub>	Weight of water per 100 c.c. of soil withdrawn from zero tension to inflexion point V <sub>z</sub> -V <sub>x</sub>	Porosity factor $\frac{V_z - V_x}{pF_x}$	Permeability coefficient of soil for water in cms/hr
N	50.44	29.5	2.15	20.94	9.74	5.95
60°C	49.97	29.0	2.20	20.97	9.53	5.60
150°C	49.96	28.5	2.18	21.46	9.84	6.25
225°C	50.09	28.5	2.18	21.59	9.90	6.80
360°C	51.26	29.5	2.13	21.76	10.22	10.70
600°C	54.37	31.5	1.97	22.87	11.61	16.90
650°C	55.07	32.0	1.98	23.07	11.65	18.65
800°C	56.11	32.0	1.95	24.11	12.37	17.45
1000°C	56.80	32.5	1.83	24.30	13.27	15.60

(1) WATER CONTENT AT ZERO TENSION (V<sub>z</sub>) : The water content at zero tension decreases slightly on heating the soil to 60°C, increase slightly up to 225°C and further increases more rapidly upto 650°C and above this temperature the increase is less.

(2) WATER CONTENT AT INFLEXION POINT (V<sub>x</sub>) : The water content at inflexion point decreases upto 60°C and further decreases slightly upto 225°C. From 225°C to 650°C it increases and above 650°C it increases less rapidly.

(3) WATER WITHDRAWN FROM SOIL FROM ZERO TENSION TO INFLEXION POINT (V<sub>z</sub>-V<sub>x</sub>) : The weight of water per 100 c. c. of soil withdrawn from zero tension to inflexion point has remained the same on heating the soil upto 60°C and has steadily increased from 60°C to 1000°C.

(4) pF OF INFLEXION POINT (pF<sub>x</sub>) : The pF of inflexion point in the pF-water curves of the normal and heated soils shows interesting changes. The pF first increases on heating the soil to 60°C and slightly decreases upto 225°C. From 225°C to 650°C the decrease is more rapid and above 650°C the decrease is less.

(5) POROSITY FACTOR  $\left(\frac{V_z - V_x}{pF_x}\right)$  : According to Baver<sup>1</sup> the porosity factor is the ratio of the amount of water withdrawn from zero tension to inflexion point and the pF of inflexion point. The porosity factor decreases on heating the soil to 60°C and then increases slightly upto 225°C. Above 225°C it increases more rapidly.

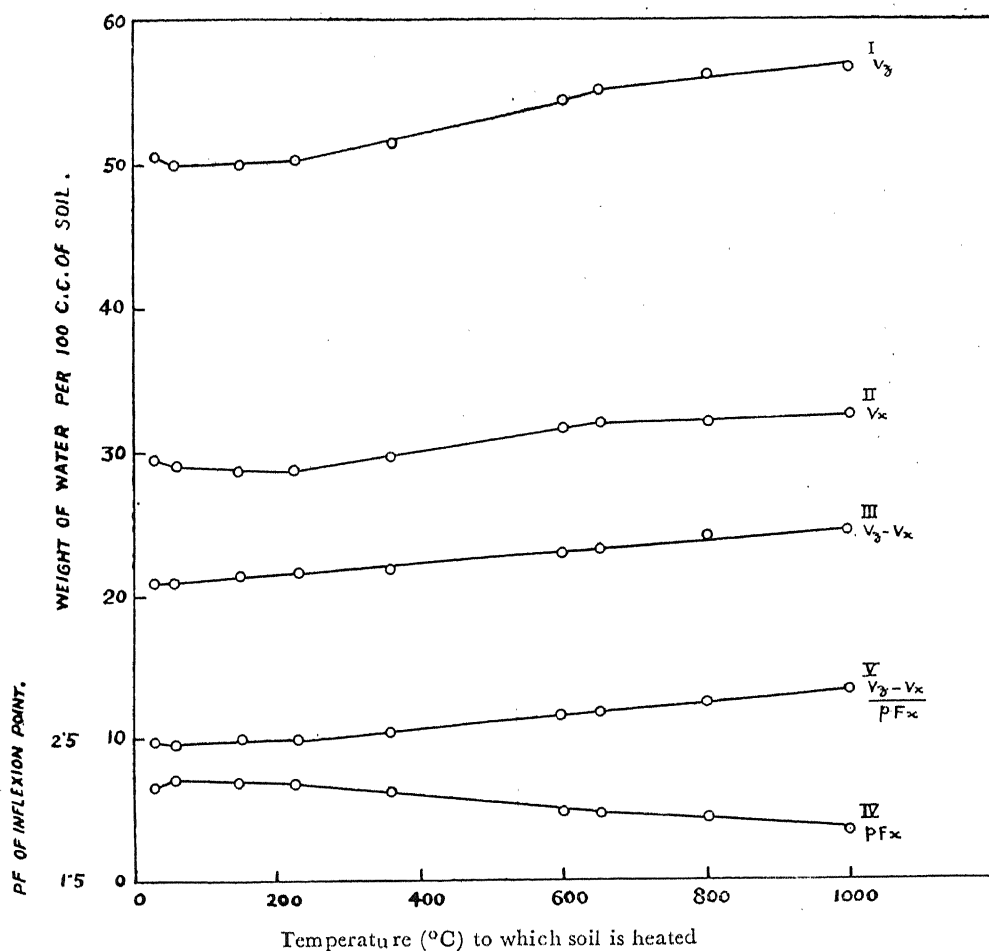


Fig. 4. Relation between the temperature to which soil is heated and  
 I. Height of water retained per 100 c.c. of soil at zero tension  $V_z$ ,  
 II. Height of water retained per 100 c. c. of soil at inflexion point  $V_x$ ,  
 III. Height of water withdrawn per 100 c. c. of soil from zero tension to inflexion point  $V_z - V_x$   
 IV. PF of inflexion point  $PF_x$ .

V. Porosity factor  $\frac{V_z - V_x}{PF_x}$

RELATION BETWEEN PERMEABILITY AND THE AMOUNT OF WATER WITHDRAWN FROM SOIL FROM ZERO TENSION TO INFLEXION POINT : Baver considers that the amount of water per 100 c. c. of soil withdrawn from zero tension to the inflexion point is equal to the volume of non-capillary pores in the soil. Non-capillary pore volume is one of the factors which determine the rate of permeability. It has been shown earlier<sup>3</sup> that the non-capillary pore volume as obtained by direct measurement of the capillary and total pore volumes varies linearly with permeability coefficient with inversion points for soils heated to 225°C and 650°C. In the present study the weight of water withdrawn from zero tension to inflexion point bears similar relation to permeability with inversion points for soils heated to 225°C and 650°C,



Fig. 5. This parallelism in the two relations indicates that the amount of water withdrawn from zero tension to inflexion point does really represent the non-capillary pore volume in the soil. The significance of the inversion point itself for soil heated to 225°C was attributed to a shift,<sup>3</sup> in the pF inflexion point in the pF-water curves and this has been shown to be true from a study of the variation in the pF of inflexion point with the temperature of heating the soil.

RELATION BETWEEN PERMEABILITY AND POROSITY FACTOR : Though the amount of water withdrawn from zero tension to inflexion point increases continuously with temperature of heating the soil, the variation of pF of inflexion point is however significant. Porosity factor being the ratio of the amount of water withdrawn from zero tension to inflexion point and the pF of inflexion point, its variation with temperature will be similar to that of pF of inflexion point but in the reverse order, Fig. 4. This curve is very similar to the curve of permeability—temperature of heating the soil, shown in the earlier paper<sup>3</sup> with respect to the inversion points. The relation between permeability and porosity factor is linear over the entire range of temperatures upto 650°C, Fig. 6. This is a very significant relation showing the dependence of permeability on the combined effects of non-capillary pore volume and the pF of inflexion point.

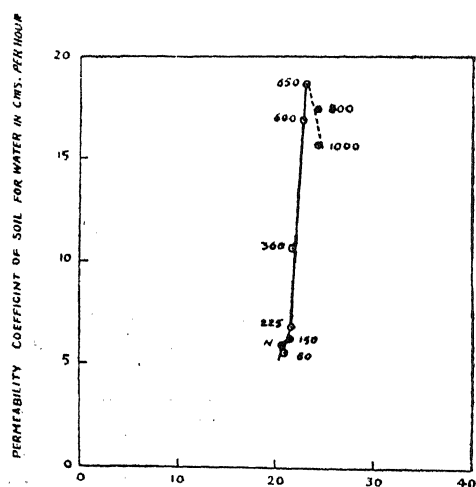


Fig. 5. Relation between permeability and weight of water withdrawn per 100 c. c. of soil from zero tension to inflexion point.

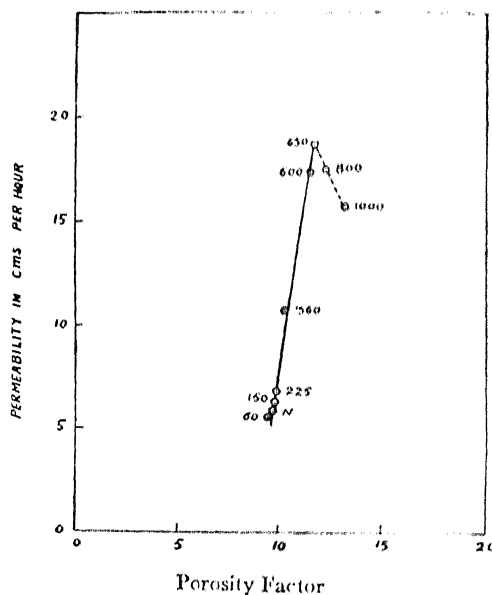


Fig. 6. Relation between permeability and porosity factor.

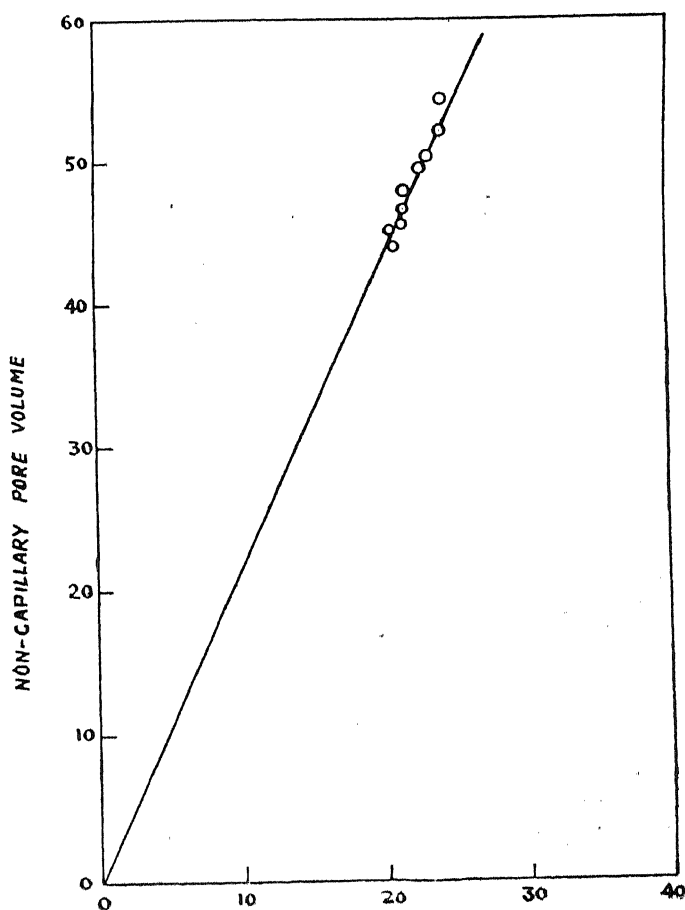
An explanation of the inversion points in the permeability—water withdrawn from zero tension to inflexion point and permeability—porosity factor curves, for soil heated to 650°C is necessary, Fig. 5 and 6. This apparent anomaly is due to the fact that the soils heated above 650°C are not stable systems. They undergo disintegrations under prolonged submergence in water.<sup>7</sup> The amount of water at zero tension, was measured after one day's contact of soil with water whereas the permeability was obtained after 7 days submergence of soil in the water.<sup>7</sup> The permeability is really that of a changed system. As such there is no meaning in extending the above two relations to soils heated above 650°C.

RELATION BETWEEN NON-CAPILLARY PORE VOLUME AND THE AMOUNT OF WATER WITHDRAWN FROM ZERO TENSION TO INFLEXION POINT : From the foregoing study and also from the investigation of Baver there is no doubt that the amount of water withdrawn from zero tension to inflexion point represents the total non-capillary pore volume. Because, this quantity increases with increase in the temerature of heating the soil (Fig. 4) approximately in the same way as the non-capillary pore volume determined by direct measurements.<sup>3</sup> Whether the amount of water withdrawn from zero tension to inflexion point is equal to the non-capillary pore volume or whether it i only a measure of it is a point which is yet to be clarified. Baver however has taken this as equal to the non-capillary pore volume but this generalization is not in harmony with what has been observed in this paper. The non-capillary pore volume determined by direct measurement is plotted against the amount of water withdrawn from zero tension to inflexion point Fig. 7. The relation is linear. The straight line graph of the two quantities may be represented by

$$y = 2.15 x$$

where  $y$  = the non-capillary pore volume

$x$  = weight of water per 100 c.c. of soil withdrawn from zero tension to inflexion point.



Weight of water withdrawn per 100 c. c. of soil from zero tension to inflexion point.

Fig. 7. Relation between non-capillary pore volume and weight of water withdrawn from zero tension to inflexion point.

The relation indicates that the two quantities are not equal and that the non-capillary pore volume is 2.15 times the amount of water withdrawn from zero tension to inflexion point. Even considering the scatter of the points owing to limited accuracy of the measurements it is definite that the two quantities are not equal because of the observed ratio of 2.15. The physical significance of this relation namely that the non-capillary pore volume is nearly twice the amount of water withdrawn from zero tension to inflexion point, is not clear.

**PHYSICAL SIGNIFICANCE OF THE pF OF INFLEXION POINT IN RELATION TO PERMEABILITY :** Though Bayer has stressed on the importance of the pF of the inflexion point as a factor in determining permeability, the physical significance of this quantity has not been elucidated. The pF of inflexion point in a soil really indicates the most predominant pore size in the soil. In a soil, the pores are to be visualised in the form of continuous channels rather than as isolated pockets. These channels have a number of constrictions producing what are known as cavities or ink bottle shaped pores. The cavity concept was first suggested by McBain<sup>2</sup>, and later elaborated by Rao, K. S. (4, 5, 10) in an extensive study of the sorption-desorption hysteresis. Hysteresis phenomenon is essentially static and is connected with equilibrium between the liquid and vapour phases.

**CAVITY CONCEPT AND PERMEABILITY :** The cavities probably play a profound role in permeability—a dynamic process. Permeability is mainly a capillary flow phenomenon. According to Poiseuille's Law, the rate of flow is proportional to the fourth power of capillary radius. As the water passes through the pores in the soil, it is really the constricted portions or the necks of the channels which offer the maximum resistance to the flow of liquid and are therefore of importance in determining the rate of flow. Assuming that the pF of inflexion point signifies the neck diameter, it follows that the pF is in a large measure, a contributory factor in determining permeability. As the neck diameter in these channels increases or decreases the permeability also correspondingly increases or decreases and the pF of the inflexion point in the pF-water curve also correspondingly decreases or increases. The pF of inflexion point in the pF-water curve denotes the most predominant pore size. According to the cavity concept if the pF of inflexion point stands for neck diameter the amount of water that can be withdrawn from the soil without changing the pF at the inflexion point appreciably represents the amount of water entrapped in the cavities.

In conclusion, the pF-water relation in the normal and heated soils is an excellent illustration of Bayer's generalizations. The physical concept of the pF of inflexion point which so far remained obscure is beautifully explained in terms of the cavity concept.

#### SUMMARY

By employing the tensiometer technique the pF-water relations has been studied in normal soil and soils heated to 60°C, 150°C, 225°C, 360°C, 600°C, 650°C, 800°C and 1000°C.

The variation with temperature of the pF of inflexion point, the amount of water withdrawn from zero tension to inflexion point and the porosity factor have been studied.

The relation between permeability and the amount of water withdrawn from zero tension to inflexion point is similar to the relation between permeability and non-capillary pore volume.

Permeability bears a linear relation with porosity factor. The exact relation between the non-capillary pore volume and the amount of water withdrawn from zero tension to inflexion point is considered.

The physical significance of the pF of inflexion point in relation to permeability is discussed. The role of the cavity concept in explaining the variation in permeability is indicated.

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# SOME CONTRIBUTIONS TO THE PROBLEM OF SOIL WATER RELATIONSHIPS

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## INTRODUCTION

Soil water is a life sustaining factor for the crop and as such has engaged the attention of workers from very early days. As early as 1897, Briggs<sup>1</sup> suggested that soil water from saturation to dryness could be designated as gravitational, capillary and hygroscopic. Later, Keen<sup>2</sup> showed that this division does not imply that the three different forms or stages of soil water are sharply distinct from each other but represent merely points on a continuous smooth curve from saturation to dryness. The present conception of soil water is based more or less on the conclusions arrived at by Keen. It may not be out of place here to recall the characteristics of gravitational, capillary and hygroscopic stages of soil water. Gravitational water is that water which drains down under the force of gravity leaving what is known as the "field capacity" in the soil. Capillary water is that water which is held in the capillaries of the soil against gravity after all gravitational water has drained down. Movement of this water takes place only by loss of water through evaporation from the ground surface or through absorption by plant roots. Hygroscopic water is that which is deposited as a thin film of condensed water vapour on soil particles when soil material is exposed to water vapour. It may be also mentioned that neither the gravitational nor the hygroscopic water is available for absorption by plants, so that it is only the capillary water which serves as the direct source of supply for plants.

Ever since its inception in 1932, the Agricultural Meteorology Division at Poona has been actively engaged in dealing with problems relating to different aspects of soil-water relationships, and obtained some interesting and useful results. The present writer has taken part in these investigations since 1937 and the object of this article is to bring to the notice of soil workers, pointedly, and in a comprehensive manner, the results obtained by the workers at Poona, with the hope of stimulating discussions and further work.

1. DIURNAL VARIATION OF THE HYGROSCOPIC WATER IN THE SOIL.—It is well-known that bare soil wetted during the rains goes on losing water during the following dry season until the surface soil is left with only hygroscopic water. After this, till the next rain, the moisture content of the surface layer of soil remains practically constant from day to day. Ramdas and Katti<sup>3</sup> showed that under the conditions described above, there is a regular diurnal exchange of moisture between the surface soil and the atmosphere. There is loss of moisture by evaporation during the day which is followed by invisible condensation of moisture on soil during the night as

if the soil exhales moisture during the day and inhales it during the night. As a result of this, although the moisture content of the soil remains more or less constant from day to day, as found by earlier workers, there is variation in the moisture content from hour to hour during the day. Later Mallik<sup>4</sup> found that not only dry soil but dry plant materials like leaves and grain also exhibit this diurnal exchange of moisture with the air layers.

In a subsequent paper, Mallik<sup>5</sup> has shown that the depth to which this diurnal exchange extends is different in different soils, being smallest in the black cotton soil and greatest in sandy soil. On the other hand, the amplitude of the exchange *i.e.*, the quantity of moisture exchanged is maximum in the case of black cotton soil and minimum in sandy soil. Table I gives the actual figures.

TABLE I

Type of soil	Depth of soil involved in the diurnal exchange of moisture (mm).	Mean maximum amplitude of variation in weight in gm. per sq. cm.
1. Black Cotton soil of Poona	10	0.0460
2. Red soil of Bangalore	20	0.0169
3. Alluvial soil of Lyallpur	25	0.0167
4. Sandy soil of Trivandrum	More than 40	0.0025

2. THE CAPILLARY ASCENT OF WATER IN SOIL AND EVAPORATION FROM THE SURFACE.—It is well-known that when a soil column is resting on a water table with the top surface freely exposed to the atmosphere, water will ascend through the soil column and evaporate from the exposed top surface of the column. The height to which water will rise will depend upon the properties of the soil and the rate of ascent will depend on the rate of removal of moisture from the top surface by evaporation. Using soil evaporimeters, designed in the Agricultural Meteorology Division at Poona, Malik<sup>6</sup> studied the ascent of water through soil columns and its loss by evaporation, using three types of soils. Time of ascent of water up to different heights in the three types of soil are given in Table II.

TABLE II

Type of soil	Time taken by water to ascend to a height of				
	6 in.	1 ft.	1½ ft.	2 ft.	3 ft.
Poona soil	1 day	2 days	6 days	15 days	not apparently wet after 6 months also.
Punjab soil	1½ days	3 days	5 days	10 days	21 days.
Bari (alkali) soil of Punjab	3 days	Not apparently wet even after 6 months.			

It was thus shown that although initially the rate of ascent is fastest in the black cotton soil of Poona, ultimately water rises up to a greater height in the alluvial soil of the Punjab while the height to which water rises in the alkali soil is strikingly low.

In the same paper, Mallik discussed the evaporation from the soil columns. He found that (1) the loss of water by evaporation goes on decreasing as the water-table recedes further and further below the surface. (2) Evaporation from the

black cotton soil and the alluvial soil is more or less similar but when the water table is near the surface, evaporation is greater from the black cotton soil, while with the water table at a distance of more than 18" below the surface, the porous alluvial soil evaporates more. (3) Evaporation from the alkali soil is very much smaller. Fig. 1 illustrates the above findings.

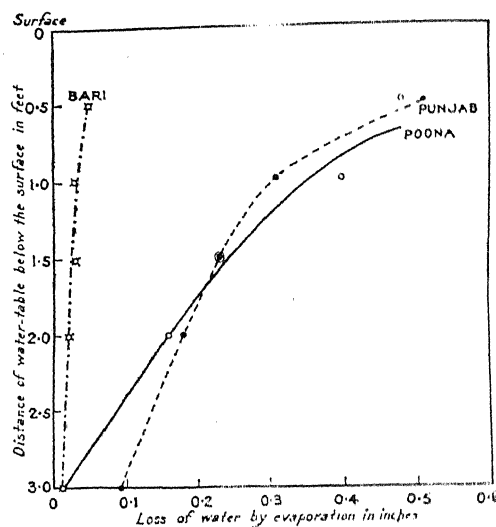


Fig. 1. Evaporation with the water-table at various depths below the surface (mean daily for May, 1939).

In a subsequent communication, Mallik<sup>7</sup> showed that the evaporation loss from the soil can be considerably reduced by the application of a thin layer of some white substance like chalk to the surface of the soil.

Using Mallik's data Ramdas<sup>8</sup> obtained the equation  $E_z = E_0 10^{-\alpha z}$  for evaporation from bare soil surface.

In this equation,

$E_z$  = evaporation with the water table at a distance of  $z$  (cm.) below the surface.

$E_0$  = evaporation when  $z$  is equal to 0

$\alpha$  = a constant different for different soils and can be determined experimentally.

$z$  = the distance (cm.) of the water table below the surface.

As  $E_0$  in the above equation is practically the same as evaporation from free water surface which can be computed approximately from meteorological factors and as  $\alpha$  can be determined experimentally, it becomes possible to obtain at least the order of magnitude of the loss of water from bare soil with the help of the above equation, if  $z$  i.e., the distance of the water table below the surface is known. The utilities of having some idea regarding the magnitude of evaporation loss from bare soil, in large scale surveys of catchment areas, are too obvious to need description.

The capillary ascent was later studied visually in small glass tubes by Ramdas and Mallik.<sup>9</sup> It was found that the rate of ascent can be represented as an exponential curve with a steep rise in the beginning and a gradual flattening latter as shown in Fig. 2.

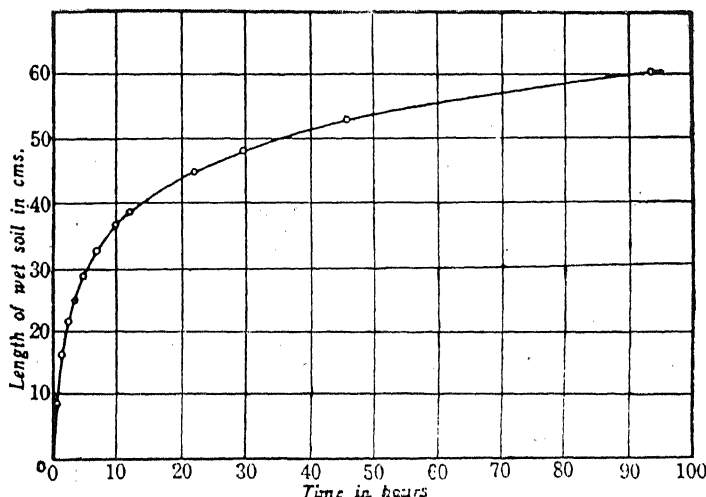


Fig. 2. Capillary ascent of water in black cotton soil of Poona.

It was also found that the ascent is initially more rapid in sand than in the black cotton soil but whereas in sand the rate slows down very rapidly, the ascent continues uniformly for a long time in the black cotton soil. The most important result obtained was however that the presence of certain salts like sodium carbonate reduces very markedly the capillary ascent of water in soils.

THE CAPILLARY ASCENT OF SOLUTIONS OF CERTAIN CHEMICAL SALTS.—As mentioned above, Ramdas and Mallik<sup>9</sup> found that certain chemical salts like Lithium and Sodium carbonates very greatly depress the capillary ascent of water containing these salts. The heights reached by water and by 2% solutions of certain salts, in the black cotton soil of Poona at the end of 26 hours, are given in Table III.

TABLE III

Nature of the ascending fluid.	Height of wet column in cm. at the end of 26 hrs.
Water	37.8
Lithium carbonate	0.0
Sodium carbonate	1.8
Sodium sulphate	35.2
Sodium phosphate	35.6
Potassium carbonate	37.8
Sodium hydroxide	40.8
Sodium borate	42.3
Sodium nitrate	43.0
Sodium chloride	43.8
Potassium hydroxide	44.7
Potassium chlorate	48.5



Having found that certain salts suppress the ascent of water in the soil they extended the investigation further to the ascent of different concentrations of sodium carbonate solution and obtained the values, given in Table IV, for the rise of sodium carbonate solutions of different strengths, at the end of 25 hours.

TABLE IV

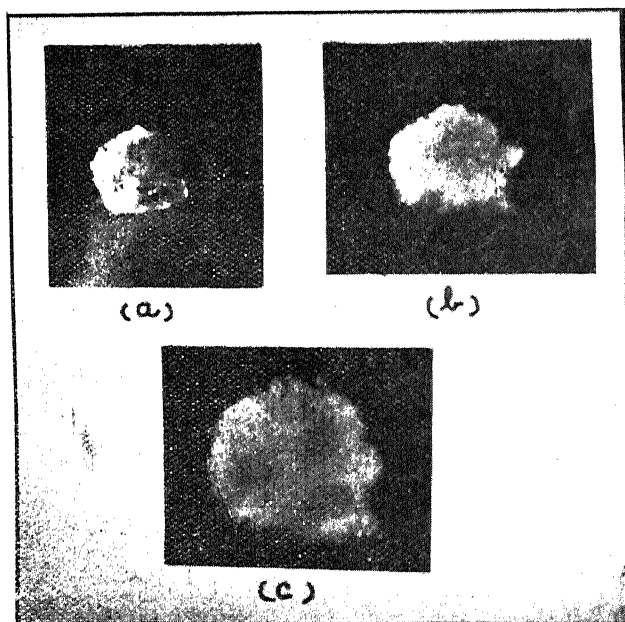
Concentration of sodium carbonate solution in water.	Ascent in the black soil of Poona at the end of 25 hrs. (cm.)
1.000 %	3.3
0.500 %	4.3
0.250 %	5.9
0.125 %	12.7
0.000 % (water)	34.3

These values showed the rapid decrease in the ascent of the solutions with the increase in the concentration of the solution although most of the effect takes place between 0 and 0.125 %. In a subsequent communication, Ramdas and Mallik and Pandit<sup>10</sup> have shown that the ascent of very dilute solutions is actually slightly greater than that of water and that the decrease in the ascent comes into effect only when the concentration is increased beyond a certain critical value which for sodium carbonate was found to be about 0.03 %.

Having confirmed that the presence of certain salts like lithium and sodium carbonates, decreases the permeability of soils. Ramdas and Mallik<sup>11</sup> examined under the microscope the action of these salts on soil particles. It was found that when a solution of these salts was added to the soil there was a very rapid and conspicuous swelling of the colloidal coating of the soil particles. Fig. 3 from the paper of Ramdas and Mallik shows the swelling of a single soil particle in a drop of lithium carbonate. Sodium carbonate also caused this swelling though the effect was less marked.

Fig 3. Swelling of a single particle of black cotton soil of Poona :

- (a) in water
- (b) 1 minute after being in saturated solution of lithium carbonate
- (c) 4 minutes after being in saturated solution of lithium carbonate



In a subsequent communication<sup>12</sup> Ramdas and Mallik reported results about the swelling caused by sodium carbonate in three different ways.

(1) 15 gr. samples of black cotton soil were shaken up with 100 c. c. solutions of sodium carbonate of different concentrations and allowed to settle. The volume of sediments after settling are given in Table V.

TABLE V

Concentration of sodium carbonate solution (per cent.)	Volume of sediment (c. c.)
0 (water)	24
0.2	29
0.4	36
0.7	41
1.0	46
1.5	41
2.0	36
3.0	32
4.0	26
10.0	22
20.0	19

The supernatant liquid at concentrations higher than 1% was coloured deep brown.

(2) The capillary ascent of sodium carbonate solutions of different concentrations was measured and found to increase slightly upto a concentration of 0.03% after which there was a very rapid fall and the ascent was minimum at a concentration of 2%. But when the concentration of the solution was increased further there was a rapid increase in the capillary ascent as will be seen from the figures given in Table VI.

TABLE VI

Concentration of sodium carbonate solution (%)	Capillary rise during 24 hrs. (cm)	Concentration of sod-carb-solu. (%)	Capillary rise during 24 hrs. (cm)
0 (water)	28.8	0.25	5.4
0.010	29.9	0.50	3.9
0.020	31.7	1.00	3.1
0.030	32.3	2.00	1.9
0.040	31.7	3.00	3.0
0.050	28.0	6.25	6.8
0.125	12.0	12.50	19.5
		25.00	26.1

(3) 100 gms. of black cotton soil was mixed with 60 c.c. of sodium carbonate solutions of different concentrations and the pastes so formed were allowed to dry

in a steam oven. The soil developed characteristic cracks, the width of which was found to be maximum at a concentration of 3 per cent. At higher concentrations the tendency to crack formation decreased and above 8 per cent. the soil after drying became powdery and porous like sand. Fig. 4 shows the appearance of the soil, treated as described above, after drying.

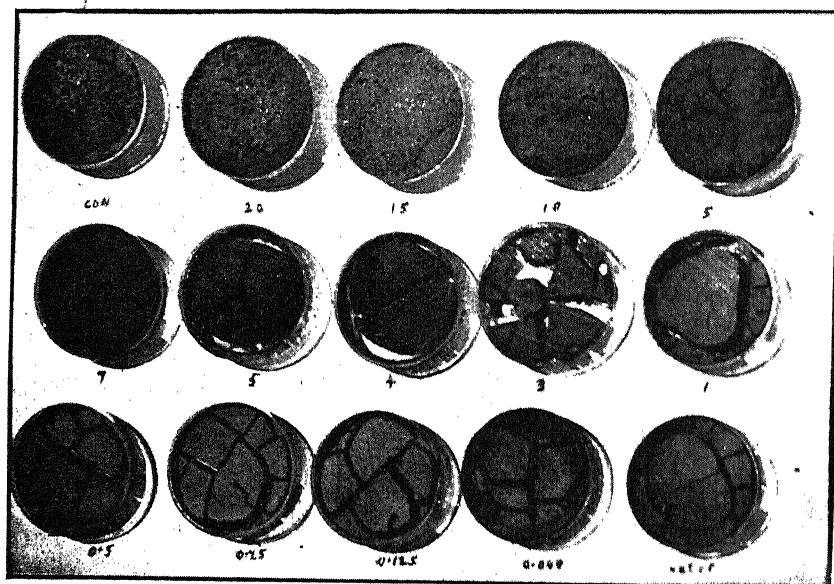


Fig. 4. Crack formation in black cotton soil of Poona wetted by sodium carbonate solution of different concentrations and dried.

In a later communication, Ramdas and Mallik<sup>13</sup> studied the effects of the swelling of soil caused by solution of sodium carbonate on permeability using Green and Ampts equation (quoted by B. A. Keen on pages 94-96 of his book "The physical properties of soil, 1931") given below :

$$\frac{P}{S} = \frac{K \log K/(K-1)-1}{t}$$

Where  $P$  = permeability of the soil,

$S$  = pore space of the soil,

$K$  = capillary force acting on the boundary of the solution.

$l$  = height to which the solution rises in time  $t$  and

$t$  = time taken by the solution to rise to height  $l$ .

For each concentration of the solution, the value of  $K$  was so chosen that the computed value of  $P/S$  remained constant for the ascent of the solution of that particular concentration for different hours. The values of  $P/S$  and  $K$  obtained are given in Table VII.

TABLE VII

CONCENTRATION OF SODIUM CARBONATE SOLUTION PER CENT.  
(GM. PER 100 C.C OF DISTILLED WATER)

	0	0.01	0.02	0.03	0.04	0.05	0.15	0.25	0.50	1.00	2.00	3.00	6.25	12.50	25.00
(water)															
<i>P/S</i>	1.21	1.21	1.55	1.99	1.48	1.36	3.04	3.25	3.24	5.48	0.19	0.33	0.50	2.01	2.44
<i>K</i>	400	411	430	434	430	397	60	15	8	5	9	16	40	80	200

The slight increase in *P/S* ratio from 0 to 1 % is obviously due to the decrease in pore space (*S*) being more rapid than that of permeability, caused by the swelling of the soil. At higher concentrations chemical action sets in, dissolving the colloidal coating of the soil particles and thus there is a sudden increase in the pore space and the *P/S* ratio shows sudden decrease (at 2%). It is also interesting to note that changes in the values of *K*, which should be a function of the capillary ascent, for the different concentrations, are in close agreement with the changes in the observed values of capillary ascent of solutions of sodium carbonate of different concentrations, given in Table VI.

4. ALKALI SOILS AND THEIR RECLAMATION.—It is well-known that there are large areas of alkali soil in our country where no crop can be grown because of the presence of too high a concentration of salts in the soil and because these soils are impervious to water, it is not possible to leach out the salts and render such land culturable. It is also known that in all such cases sodium carbonate is always one of the salts present. The effect of sodium carbonate in making soils impervious to water is also well-known. As early as 1939, Puri<sup>13</sup> had shown that a lining of sodium carbonate along the beds of canals prevents the seepage of water. Nevertheless, as the result of the intensive experiments described above Ramdas and Mallik were able to give a clear picture of the exact way in which sodium carbonate makes the soil impervious to water. It was shown that sodium carbonate brings about a swelling of the colloidal coating of the soil particles. At very low concentrations (upto 0.03%), the incipient swelling merely reduces the diameter of the soil capillaries thus increasing, though ever so slightly, the capillary ascent. With further increase in the concentration (0.03-2.00%) of sodium carbonate rapid increase in the swelling takes place which brings about the choking up of all the pore space, making the soil impervious to water. At still higher concentrations (2.25%) chemical action sets in and the swollen colloidal mass gets dissolved in the strong sodium carbonate solution so that only the mineral pores of the soil particles are left and the soil becomes porous like sand, allowing free movement of fluids.

Having obtained as clear and complete understanding of the various effects of sodium carbonate in soils, the workers at Poona turned their attention to developing methods for the reclamation of alkali soils by restoring the permeability and thus making it possible to leach out the salts. Ramdas and Mallik<sup>14</sup> showed that a solution of sodium chloride restores the permeability of the black cotton soil, rendered impervious by sodium carbonate. They also found that the naturally occurring alkali soil of the Punjab known as "Bari" although impervious to water is pervious to a solution of sodium chloride. However, it was found that the restoration of the permeability by sodium chloride solution is only temporary and even after the alkali soil is thoroughly washed with sodium chloride solution it continued to remain impervious to water.

Extending the investigations further, Katti<sup>15</sup> studied the effects of different chloride solutions on the permeability of alkali soils. He found that those chlorides whose corresponding carbonates are insoluble in water can restore the permeability of alkali soils permanently *i.e.*, Calcium, Strontium, Barium and Magnesium chlorides were found to restore permanently the permeability of alkali soils.

The values obtained by Katti<sup>15</sup> for the percolation of water through a column of 'Bari' (alkali) soil of the Punjab after the soil was leached by solutions of different chlorides are given in Table VIII below :

TABLE VIII

Percolation of water through 25 cm. layer of the 'Bari' soil treated with

Time	Water	5%LiCl Soln.	5%NaCl Soln.	5%KCl Soln.	5% NH <sub>4</sub> Cl Soln.	5% CaCl <sub>2</sub> Soln.	5% SrCl <sub>2</sub> Soln.	5% BaCl <sub>2</sub> Soln.	5% MgCl <sub>2</sub> Soln.
Days									
1	0.1	10	10	10	12	30	30	35	30
2	0.2	15	15	15	17	60	60	70	60
3	0.3	17	16	18	22	90	90	105	90
4	0.4	18	17	20	27	120	122	137	120
5	0.5	19	18.5	22	21	150	152	172	150
6	0.6	19.5	19.0	23	35	180	184	207	180
7	0.7	19.7	19.2	24	39	210	216	242	210
8	0.8	19.9	19.4	25	43	240	250	277	240
9	0.9	20.1	19.6	26	47	270	280	309	270
10	1.0	20.3	19.8	27	51	300	315	344	300
12	1.2	20.5	20.0	28	57	360	375	414	350
14	1.4	20.7	20.2	32	63	420	435	484	400
16	1.6	20.9	20.4	34	69	470	480	554	450
18	1.8	21.1	20.8	36	75	520	530	614	500
20	2.0	21.3	21.3	37	80	640	650	754	620
25	2.5	21.8	21.5	41	95	700	710	827	680
30	3.0	22.3	22.2	45	110	760	770	900	740

It will be seen from the table that at the end of 30 days although the percolation of water was only 3.0 c. c in soil previously washed with water, it was as high as 900 c. c in the case of the soil previously treated with a 5% solution of barium chloride and 760 c. c in soil treated with calcium chloride. It is thus clear that by treatment with chlorides of calcium, strontium, barium or magnesium, the 'Bari' soil, normally impermeable, becomes permeable to water. It is obvious that the sodium carbonate present in the 'Bari' soil reacts with the chlorides forming corresponding carbonates which being insoluble cease to have any further effect when water is added to the soil, which no longer contains sodium carbonate. Thus there is no swelling and no choking up of the pore space so that the free movement of water is not obstructed. The sodium chloride, formed in the process, can now be freely washed out and the soil rendered fit for growing crops. It is seen thus that by treating alkali soil with chlorides of calcium, strontium, barium or magnesium and then washing out the sodium chloride formed, alkali soils can be quickly reclaimed. Taking into consideration the cost of the material, it would be most economical to use calcium chloride for this purpose.

Pot culture experiments with 'Bari' soil conducted at the Agricultural Meteorology Division at Poona have confirmed the above method of reclamation of alkali soils using calcium chloride.

It may be of interest here to recall that the use of calcium sulphate (gypsum) for the reclamation of alkali soils is well-known from quite a long time. However, it is certain that in view of the high solubility of calcium chloride, the use of this salt instead of gypsum will make the process of reclamation very much quicker. The present writer hopes that the method of reclaiming alkali soil with the help of calcium chloride will be considered to be well worth trial and field experiments will be conducted by Agriculturists in India in the near future.

In conclusion, the present writer wishes to express his sincere thanks to all the workers at Poona whose results have been made use of in preparing this article.

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## SOIL AS AN ENGINEERING MATERIAL.

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(Communicated by Prof. S. Ghosh)

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With the development of science of soil, in addition to the single value constant, other physical constants such as Atterbergs limit (liquid and plastic limits) soil shrinkage, and Proctor's value has been found out.

Fundamental properties of soil have been made use of in the electro-osmotic stabilisation of soil which has been receiving particular attention for stabilising natural slopes and excavations in fine grained soils. Geological properties of cohesive soils have been found to give a practical solution to the foundation problems in preference to other soil mechanics tests. In the manufacture of bricks and tiles also the plastic properties of clays influences the process to a considerable extent.

The properties of the soils depend upon the clay minerals present in them. In addition to the characteristics mentioned above, X-Ray diffraction and differential thermal analysis methods have been employed to determine its mineralogical compositions which in turn governs the physical properties of soil to a great extent.

### UTILIZATION OF SOIL.

**STABILIZATION.**—Soil has been used as a building material. The moment it comes in contact with water its strength decreases considerably on account of the lubricating action of water molecules round the soil particles. Attention of scientists was focussed on how to reduce the ingress of water into soil mass whereby the trouble could be avoided.

**MECHANICAL STABILISATION.**—Well graded soil when compacted at its optimum moisture content gives maximum density, and walls made of such compacted soil with any stabilizer can stand weathering fairly well as compared with soil alone. This soil can be used as a walling material in two ways. (i) by turning into blocks of suitable size, e. g., 16" × 12" × 8" (ii) by constructing monolithic walls (iii) putting the moist soil into wooden shutterings and compacting to give a wall of about 10-12" thickness. This soil can be made further resistant by the addition of stabilising agents such as cement. Such walls are largely used in the arid regions of America for farm houses, stores and low cost housing. In India during and after war years, to meet the scarcity of housing, various housing agencies tried to speed up building construction using stabilised compacted soil.

### CEMENT STABILISATION

The Portland Cement Association of America have carried out extensive research work in this field using cement as a stabiliser for soil. It has been shown that soils

which are not too clayey can be successfully stabilised using a proportion of cement upto 10 per cent. Blocks of soil cement, besides standing upto weathering tests give a compressive strength as high as 1000 lb/sq. in. after seven days of curing. About 400 houses have been built in 12 different places in Punjab for the refugees from Pakistan, using this technique.

#### BITUMEN STABILISATION

Bitumen is another well-known stabiliser. It imparts a water-proofing property to the soil. It is used either in the liquified form, as a solution or as an emulsion. A good number of houses made with soil blocks stabilised with bitumen, named 'bitudobe,' have been constructed in the agricultural areas of the U. S. A. Sand bitumen carpets have been used extensively during World War II as a base for the air-field runways. Kutchia house constructed by Punjab P.W.D. at Hirakud with soil bitumens plaster has come out efficient to withstand weathering effect.

#### OTHER STABILISERS

Some industrial wastes like sulphate liquor from paper mill have also been tried with partial success. This institute has met with success on laboratory scale in lime sludge which is another waste from sugar factories; nearly 2 per cent of this material mixed with 3-5 per cent. of commercial sodium silicate stabilises the soil effectively.

#### WATER-PROOFING TREATMENT AND RENDERINGS ON WALLS

Among the water-proofers, soap of fatty acids such as sodium stearates have been used. Vinsol resin and soil stabilising oil have also given satisfactory results.

Application of suitable plasters on stabilised soil walls is not very easy, as the wall and cement do not adhere owing to the diversity in the nature of the material. Surkhi plaster has successfully been tried on such walls which is reported to have behaved satisfactorily without being detached from the wall surface. Bituminised plasters are also used, but owing to their black colour they are not very popular. When katcha bricks are used the bottom portion (one or two feet) of the wall is usually built in pucca bricks. It has been observed that in areas where good quality bricks are available at a reasonable price say *e. g.*, Rs. 25/- 30/- per 1,000, the stabilised wall construction does not pay but proved economical in places where the cost of ordinary bricks are about Rs. 60-70 and where rainfall is more than 15-20".

#### FOUNDATION ON EXPANSIVE CLAYS

Foundations in alluvial soil and in soils where the sound rock is available near the ground level, normally no difficulty is experienced in the building of of the same. However, the problem is quite different and complicated when the substratum consists of a highly expansive soil which swells in rainy season and shrinks in dry season. Many a building have cracked as a result of this. Such failure in building construction is mostly due to unequal settlement of foundation. In South Africa, Australia and certain parts of America, where similar clays are found, considerable research work has been carried out on the foundation problems. This Institute has set up two field sites, one at Hoshangabad and other at Indore, to record the vertical movement of ground at various depths and locate the depth at which the movement of ground is negligible.



## BRICKS AND TILES

Clay, particularly burnt clay, is one of the oldest of building materials and ranks with timber as the most widely used. The clay, when well burnt is most durable building material known and has many other advantages such as dimensional stability and attractive appearance, over many of its modern competitors. About 500 crores fired bricks are manufactured in India annually in the organised brick fields. 75 % of this total output is produced in the north where very suitable alluvial soil is available for making bricks.

Recent work has shown that burnt clay can be used in building in new forms and it is certain that, provided the industry is prepared to adapt itself to changing conditions and to take advantage of the results of research, clay will remain one of our most important building materials. However such developments required a detailed knowledge of the properties of the clays. Developmental work carried out at this Institute has brought out the following results :

- (a) By suitably modifying the mechanical composition of the raw material the shrinkage can be controlled to a considerable extent. By this method, it is also possible to get bricks of high crushing strength of, say 7000 lbs. per sq. in., as against ordinary Indian bricks which have a strength ranging from 500 to 2000 lbs. per sq. in.
- (b) Preliminary trials have shown that, in the bricks made of black cotton soils of the Bombay-Deccan areas, the crushing strength does not change much over a wide range firing temperature. It appears that the firing of such bricks can be made at lower temperatures and with fuel of less calorific value or with a lesser quantity of fuel. Improvements in the strength could be effected by grinding the black cotton soil for a period of 1-2 hours in edge runner mill. Grinding after incorporation of certain amount of coal ash also improved the properties considerably.
- (c) The study of fluxes present in the brick earths was also undertaken. This may help in finding methods of preventing the warping of bricks made of black cotton soil, during the firing process.
- (d) After laboratory experiments had been carried out successfully Sindri ash was used in small proportions as an admixture to the usual raw material in actual production. Such bricks have been fired in local kilns under ordinary factory conditions, along with other bricks in order to find out how the quality of bricks could be improved.
- (e) Textural diagrams have thrown more light on the current practice of selecting brick earths around Roorkee. For the alluvial soil around Roorkee, maximum strength obtained at 30 per cent each of silt and clay, when bricks were fired at 1000°C.

Further work on the improvement of bricks from alluvial soil and bricks from black cotton soil track is in progress.

### SURKHI

Surkhi-lime mortar is very well known and has been used in large scale construction in the last century in the major engineering works in this country

*e. g.* the large network of canals in North India. During recent years owing to the construction of large river valley projects an impetus has been given to the use of this material and attention has been paid to its standardisation and quality control. The quality of surkhi will depend greatly upon the mineralogical composition of the soil, the firing temperature and the particles size and it is hoped that it will be possible within a short time to lay down standards for surkhi made from each of the main groups in the country.

#### LIGHTWEIGHT CLAY AGGREGATES

Certain clays and shales have the property of "Bloating" or expanding when burnt, at temperatures between 1000-1300°C and by a suitable treatment it is possible to produce an aggregate having a bulk density of one-third to one-half that of ordinary crushed rock or gravel aggregate, concrete made from this aggregate has a density of only from one-half to two-thirds that of concrete made from ordinary aggregate but the strength is adequate for all normal purposes. The use of such concrete in buildings and bridges results in considerable decrease in dead weight with resultant reduction in the cost of the structure.

This work on lightweight aggregates is of very great importance to the building industry. It is not generally realised that the weight of a multi-storey building is about five times greater than the live load for which it is designed. It has been found in U. S. A. that by using lightweight concrete for floors dead loads can be reduced by about 40 per cent. saving something like 20 per cent. in the steel required and reducing the overall cost by about 10 per cent.

#### CONCLUSION

It will be seen from the foregoing short description that soil can find large scale use in the building industry. However, it is desirable that a good deal of coordination exists among the soil workers whether in the field of agronomy or in soil engineering. Under the auspices of the Indian National Society of Soil Mechanics and Foundation Engineering and Central Board of Irrigation and Power, a good deal of work on the study of physico-chemical properties and mechanics of soil is being done. It is desirable that other soil scientists working on fundamental properties of soil are also associated with this body so that they are able to help each other to solve the complex problem of soil science. It cannot be forgotten that the pioneering preliminary work to probe into the properties of soil has been carried out by soil scientists. The modern soil engineers can always draw up all the available information and try to use it to meet their requirements. A body such as this would be in a better position to bring about this coordination between the soil scientist and the soil engineer.

# SHRINKAGE LIMIT OF SOILS

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(Communicated by Dr. S. P. Mitra)

(Received on 29th October, 1954)

The shrinkage limit of a soil, according to Knight<sup>3</sup> is the moisture content, expressed as a percentage by weight of the oven-dried soil, at which a reduction in moisture content will not cause a decrease in volume of the soil mass, but at which an increase in moisture content will produce an increase in the volume of the soil mass. It is calculated from :—

$$\text{S. L.} = \frac{M - (V - V_o) \times 100}{W_o} \quad \dots \quad (i)$$

where S. L. = Shrinkage limit.

M = Moisture percentage of the wet soil pat on the weight of the oven-dried soil.

V = Volume of wet soil

V<sub>o</sub> = Volume of the dry soil pat

W<sub>o</sub> = Weight of the oven dried soil pat.

Fig. (I) shows the shrinkage curves of a few typical soils. The soil volumes are plotted against the volume of water present. The mechanical analysis of the soils was as follows :

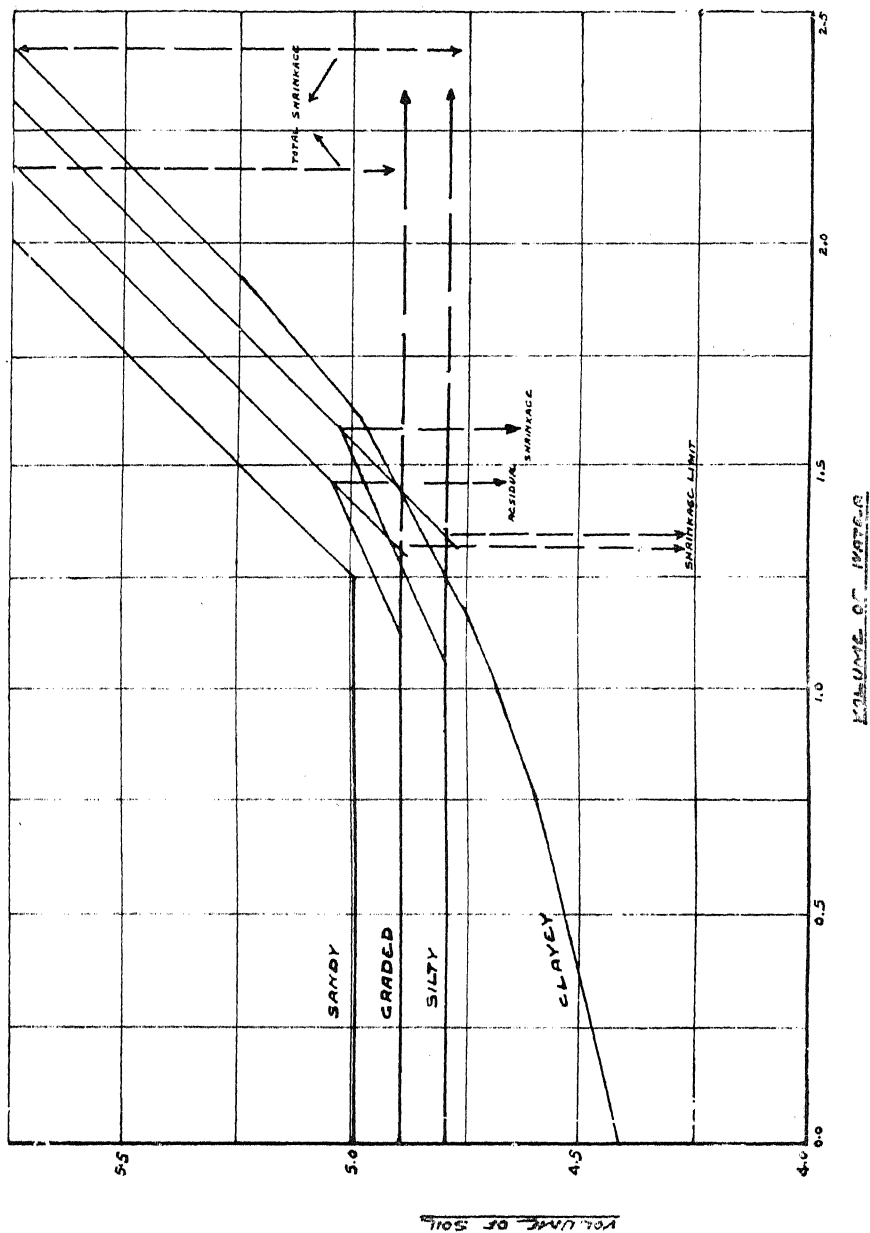
S. No.	Soil Classification	Sand %	Silt %	Clay %
1.	Sandy	88.0%	18%	4.0
2.	Sandy loam (graded)	70.0	18.6	12.1
3.	Silty	15.00	68.5	16.4
4.	Clayey (Bentonite)	4.0	8.6	86.9

All the curves are parallel in the wet region and have a slope of unity. On further dehydration, the decrease in soil volume is less than the volume of water evaporated. This inflexion indicates the point at which air enters the soil. The shrinkage in the lower portion of the curve is called residual shrinkage, as distinguished from total shrinkage (Haines<sup>2</sup>). The total shrinkage of soils varies with the percentage of the clay content. But the residual shrinkage seems to be dependent upon the hydration of the colloidal material, both organic and inorganic. This is confirmed by the clayey soil (Fig. I) having the greatest residual shrinkage as compared with the other soils. The clayey soil is a Bentonitic clay. The graded soils according to Dhawan<sup>1</sup> for Kaolinite type of soils is as follows : —

Clay (particles less than .002 m.m.)	... 8 to 15 %
Silt (particles greater than .002 m.m. but less than .02 m.m.)	... 12 to 25%
Sand (particles greater than .02 m.m. but less than 2.0 m.m.)	... 60 to 80%

FIG. NO. I

# SHRINKAGE CURVES OF VARIOUS TYPES OF SOILS



The first part AB, A'B', A''B'', A''',B''', represents the stage when decrease in moisture is accompanied by an equal decrease in volume. Therefore the curve makes an angle of 45° with the X-axis. The inter-section of this line drawn through the point of minimum volume represents the shrinkage limit (Fig. 1).

A glance at the curves shows that the moisture content below which there is no decrease in volume with the decrease in moisture content is the point at which the curves become horizontal to the X-axis. Therefore this point should represent the true shrinkage limit and not the point obtained as discussed in the preceding paragraph. The values of shrinkage limit as determined from the equation (i) will always be a little higher than the real values.

From the above discussion, it is concluded that for the determination of exact value of shrinkage limit of soils, the curves between soil volume and volume of water or volume for 100 gms. of soil and moisture percentage should be plotted. The point at which the curve becomes horizontal represents the true shrinkage limit of the soil.

#### SUMMARY

(i) Shrinkage limit is the moisture content at which the curve between the volume of water and volume of soil or moisture percentage and volume of soil per 100 gms. becomes horizontal.

(ii) The values of shrinkage limit as determined by the well-known formulae

$$S. L. = M - \frac{(V - V_0)}{W_0} \times 100$$

are a little higher than the true values.

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## MOVEMENT OF MOISTURE UNDER UNSATURATED PHASE PART I.

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The movement of water through the soil pores takes place either by the action of gravity or by capillary forces alone or in combination. But the type of water movement is mainly governed by the dominance of the moving force. It may be discussed from the following two points of view :—

(a) MOVEMENT IN SATURATED SOILS.—The water moves in the larger pores under the action of gravity. It occurs in sufficiently large quantities to obey the ordinary laws of hydraulics.

(b) MOVEMENT IN UNSATURATED SOILS.—This movement takes place primarily through capillary forces from surface to surface or in the small pores in the presence of numerous air-water interfaces and the dominant force in such movements is the capillary potential.

The movement of water by capillary action has interested soil scientists for a long time. Keen<sup>5</sup>, Buckingham<sup>2</sup>, Gardner<sup>3</sup>, Wollny<sup>4</sup>, Loughridge<sup>7</sup>, King<sup>6</sup>, and Harris and Turpin<sup>1</sup> studied various factors governing the capillary movement of water in soil. According to the modern concept the rate of capillary flow of water through soil is given by the equation.<sup>1</sup>

$$Q = - K \text{ Grad } \psi$$

where  $Q$  - Mass of water which passes in one second through one square centimeter of an imaginary plane perpendicular to the direction of flow.

$K$  = Capillary Conductivity

$\text{Grad } \psi$  = Capillary potential gradient.

$K$  depends upon the kind of soil, its degree of packing, temperature, and the moisture content.

Richard<sup>8</sup> approached the problem of the movement of water in an unsaturated soil from the principles of hydraulics. Another simple analogy is to compare the capillary potential with the thermal or temperature potential in the flow of heat through a metal bar.

An attempt has been made in this paper to develop a simple equation for the soil moisture system in an unsaturated phase and to determine the value of  $K$  experimentally.

## THEORY OF MOVEMENT OF MOISTURE IN UNSATURATED SOILS

The movement of moisture may be represented by a general equation :—

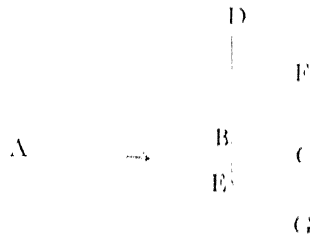
$$Q = K A \frac{dM}{dS} \quad \dots (1)$$

where  $Q$  = Discharge  
 $A$  = Cross sectional area of flow  
 $M$  = Moisture content

$$\frac{dM}{dS} = \text{a measure of the force causing the flow.}$$

The capillary potential depends upon the soil type, temperature, its compaction and moisture content. If the three former factors are fixed, the moisture content becomes a measure of capillary potential.

The general equation of moisture movement in two dimensions in an unsaturated soil is derived as follows :—



Let A B C be a line of flow and let A B =  $S$  and A C =  $S + dS$ .  
 DEGF may be considered a small volume and the cross sectional area of the faces represented by DE and FG may be taken as  $A$ .

If the moisture content at the face DE at a given instant =  $M$

Moisture content at the face FG =  
 $= M + G \cdot dS$

Where  $G$  = Moisture gradient

$$= \frac{dM}{dS} \text{ (in the direction of flow at D E)}$$

Discharge at the face DE from the equation ..... (i)

$$Q = KA \frac{dM}{dS} \quad \dots (ii)$$

Discharge leaving the face F G

$$Q + dQ = KA \frac{d}{dS} (M + G dS) \quad \dots (iii)$$

Subtracting (iii) from (ii) we get

$$\begin{aligned} dQ &= KA dS \cdot \frac{dG}{dS} \\ &= KA \cdot dS \cdot \frac{d^2M}{dS^2} \quad \dots (iv) \end{aligned}$$

$$\text{as } G = \frac{dM}{dS}$$

Volume of soil within DEGF

$$= A dS \quad (\text{Since } A = \text{Cross-sectional area} \\ \text{and } dS = \text{distance BC})$$

Therefore the rate of change of moisture content within DEGF with time is given by

$$\frac{dQ}{dS} = K A \frac{d^2 M}{dS^2} \quad (\text{From equation (iv) ... (v)})$$

or

$$\frac{dQ}{A \cdot dS} = K \cdot \frac{d^2 M}{dS^2} \quad \dots \text{(vi)}$$

This is the differential equation of moisture movement.  
One form of the solution of the equation is

$$M = e^{kt} \frac{d^2}{dx^2} f(S)$$

Where

$f(S)$  is an arbitrary function of  $S$ .

Expanding the differential operator we have

$$M = f(S) + Kt \cdot \frac{d^2 f}{dS^2} + \frac{K^2 t^2}{2!} \cdot \frac{d^4 f}{dS^4} \\ + \frac{K^3 t^3}{3!} \cdot \frac{d^6 f}{dS^6} + \dots$$

Let us take another mode of attack

We know

$$\int_{-\alpha}^{\alpha} \frac{e^{-u^2}}{c} du = \pi^{\frac{1}{2}}$$

writing  $(U - l)$  for  $U$ , where  $\rho$  is independent of  $U$

$$\int_{-\alpha}^{\alpha} \frac{e^{-u^2} + 2ul}{c} du = \pi^{\frac{1}{2}} \cdot c$$

Applying this method for the solution of the equation

$$\frac{dM}{dt} = K \cdot \frac{d^2 M}{dS^2}$$

we have as before

$$M = e \left( \sqrt{Kt} \frac{d}{dx} \right)^2 f(S)$$

where  $f(S)$  is any arbitrary function independent of  $t$

$$\text{Replacing } l \text{ by } K^{\frac{1}{2}} t^{\frac{1}{2}} \frac{d}{du}$$

in the foregoing formula in equivalent operators, we have

$$M = \frac{1}{\pi} \int_{-\alpha}^{\alpha} \frac{e^{-\mu^2} + 2\mu \sqrt{Kt} \frac{d}{du}}{c} f(s) d\mu \\ = \pi^{-\frac{1}{2}} \int_{-\alpha}^{\alpha} e^{-\mu^2} f(S + 2\mu K^{\frac{1}{2}} t^{\frac{1}{2}}) d\mu$$



Let  $S + 2\mu K^{\frac{1}{2}} t^{\frac{1}{2}} = \lambda$   
then M becomes

$$= \frac{1}{2 K^{\frac{1}{2}} \pi^{\frac{1}{2}} t^{\frac{1}{2}}}$$

$$= \frac{1}{2 (K \pi t)^{\frac{1}{2}}} \int_{-\alpha}^{\alpha} e^{-\frac{(S-\lambda)^2}{4 K t}} f(\lambda) d\lambda$$

Now  $f(\lambda)$  is an arbitrary function, if we choose to assume its value to be zero everywhere except where  $\lambda = t$  and then write

$f(\lambda) d\lambda = H$  We have

$$M = \frac{H}{2 (K \pi t)^{\frac{1}{2}}} e^{-\frac{(S-\lambda)^2}{4 K t}}$$

$$= \frac{H}{2 \sqrt{K \pi t}} \text{ as a particular solution.}$$

$$\text{or } K = \frac{H^2}{4 \pi t M^2} = \lambda \frac{S^2}{t}$$

$$\text{Which is of the form } K = \frac{1-p}{1+p} \cdot \frac{S^2}{t}$$

Because M is the moisture content expressed as a percentage of soil volume or weight.

The above equation can also be derived as follows :

$\updownarrow$ S, M + dM	M + p. dM
$\updownarrow$ S, M - dM	M - p. dM

MOISTURE DISTRIBUTION BETWEEN TWO CYLINDERS.--Let the cross-sectional area of each cylinder be A,

Thickness of the soil in the two cylinders compacted at the same density and temperature but different moisture content = S

The two cylinders are joined closely and the other surfaces are sealed to protect them from the affects of evaporation. After the lapse of time T, the cylinders are separated and the moisture contents are determined separately in each cylinder.

Let the final moisture content in each cylinder

$$= M + p. dM \text{ and } M - p. dM.$$

Initial moisture gradient between the centres of the two cylinders

$$= \frac{(M + dM) - (M - dM)}{S} = \frac{2 dM}{S}$$

Final moisture gradient between the centres of the two cylinders.

$$= \frac{(M + p \cdot dM) - (M - p \cdot dM)}{S} = \frac{2 p \cdot dM}{S}$$

Average moisture gradient during the time T

$$= \frac{1}{2} \left( \frac{2 p \cdot dM}{S} + \frac{2 dM}{S} \right) = \frac{dM}{S} (1+p)$$

But  $Q = K \cdot A \cdot \frac{dM}{dS}$

Where  $\frac{dM}{dS}$  = Moisture gradient.

Substituting  $\frac{dM}{S} \cdot (1+p)$

an average moisture gradient as calculated above for

$\frac{dM}{dS}$ , we get

$$Q = K \cdot A \cdot \frac{dM}{S} (1+p)$$

But the moisture content in either cylinder has altered by  $dM(1-p)$  within a time T

$$\therefore Q = \frac{dM(1-p)}{T} \times \text{Cross-sectional area} \times \text{thickness of the soil.}$$

or  $Q = \frac{dM(1-p)}{T} \cdot A \cdot S$

Equating the values of Q we get

$$K \cdot A \cdot \frac{dM}{S} (1+p) = \frac{dM(1-p)}{T} \cdot A \cdot S$$

$$\text{or } K = \frac{1-p}{1+p} \cdot \frac{S^2}{T}$$

#### EXPERIMENTAL

The following investigation was carried out (i) To determine the value of K for soils containing varying percentages of clay.

A typical Punjab soil containing 17.0 per cent clay was dried, powdered and passed through a 2m.m. sieve. A known amount of moisture was added and the soil was well mixed in order to have a uniform moisture all round. The moisture content of the moist soils was determined and it was compacted

to a dry bulk density of 1.5 in a glass tube of about 1.0 inch diameter and 6.0" long, while in another similar glass tube the same soil was compacted at the same density but at a lower moisture content. The two tubes were placed face to face making a complete contact. All the sides were waxed thoroughly to prevent any loss of moisture due to evaporation. The tubes were kept in the horizontal position for one day after which they were separated and moisture estimation was carried out.

#### DISCUSSION OF RESULTS

The following table gives the values of K for the soils containing varying percentages of clay.

S. No.	Clay (particles below % 0.002 m. m.)	Average value of K
1.	17.0	0.28
2.	9.0	0.36
3.	6.0	0.37

The value of K was comparatively smaller for a soil containing higher percentage of clay. K represents the power of soils to transmit moisture under the given conditions. Gardner (3) has used the term 'Capillary transmission constant' to denote the capillary conductivity of soils. He has related this constant with the effective radius of the particles and the porosity of the soil.

From the above discussion it may be inferred that the movement of the moisture in soils under unsaturated conditions is determined by the driving force or potential gradient which may be expressed by a single value constant K. How the value of K is affected by the different soil conditions is being discussed in a subsequent paper.

#### SUMMARY

(i) A simple mathematical derivation of the theory of the movement of moisture under unsaturated conditions based on the potential gradient has been developed where

$$K = \frac{1-p}{1+p} \cdot \frac{S^2}{T}$$

p, S and T having the significance explained in the paper.

(ii) The value of K seems to be greater for sandy soils as compared with the clayey soils.

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## A COMBINATION PIPETTE-HYDROMETER METHOD FOR THE MECHANICAL ANALYSIS OF SOILS (POUCHI-HYDROMETER)

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The conventional reference method of mechanical analysis of soils is the so-called pipette method<sup>1</sup>. The draw-back of the pipette method, which has brought about the increased usage of less accurate methods based mainly on hydrometer measurements in settling suspensions, is its inapplicability to use in field-laboratory work for mass-scale analyses, since delicate and expensive equipment—analytical balances, temperature-controlled drying ovens—are needed for this method. This excludes the use of the pipette method in large soil surveys required for land use planning and land development schemes, and the method has been relegated to serve merely as a check-method.

Experience with most soils of the Middle East—which are almost invariably calcareous, often contain gypsum and also on this account present analytical difficulties—has shown the impossibility of any correlation between the standard pipette method and any method using different principles, notably the various direct-reading hydrometer methods. The reason for this are obviously: apart from the mentioned difficulties—the various extremely non-rigorous assumptions involved in the direct-reading hydrometer principle.<sup>2</sup> The following, completely unpredictable errors are introduced when measuring settling suspensions by a directly inserted hydrometer :

1. The suspension is stirred and turbulence is created by the insertion and by the subsequent motions of the hydrometer bulb within the settling suspension ;
2. The position of the hydrometer bulb within the column of settling suspension, and thus the locus of the measured density, are undefinable ;
3. Settling soil particles accumulate on the shoulders of the hydrometer bulb and bias the true reading, or otherwise slide down continuously or intermittently and cause "turbidity convection currents" within the sedimentation column ;
4. The space underneath the hydrometer bulb is deprived of over-head supply of settling soil particles ; failing such replenishment the density of the suspension there soon becomes less than the density of the suspension surrounding the hydrometer bulb or even of the suspension superjacent to the bulb ; this, of course, leads to instability and intermittent strong currents within the sedimentation column as can be observed by introducing coloured indicators into the suspension ; thus, normal sedimentation cannot take place in the presence of a hydrometer in a suspension.

The author has contrived to eliminate the above-listed disadvantages of pipette and hydrometer methods and to combine their advantages by developing a special pouch-hydrometer to be used in conjunction with the conventional pipette method. Thereby, the gravimetrical operations in the latter are eliminated altogether thus speeding it up and dispensing with the necessity of delicate laboratory equipment and skilled technicians. A photograph of this cheap and easily-built device—the pouch-hydrometer—is shown in Fig. 1 and a sketch of it in Fig. 2 ; a description of its construction and operation is given in the following :—

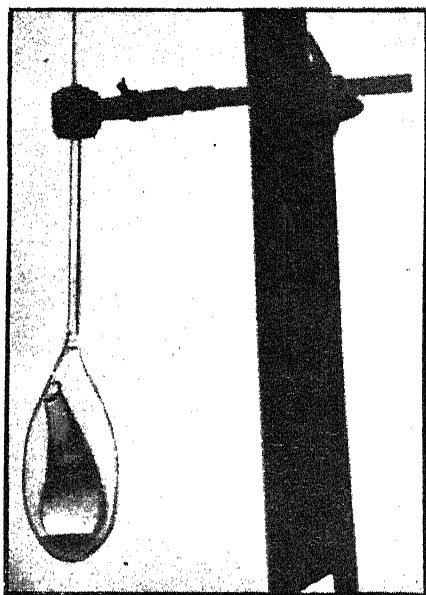


Fig. 1 POUCH HYDROMETER

#### CONSTRUCTION OF THE POUCH-HYDROMETER :

This instrument is, in some way, an adaption of the classical Nicholson hydrometer, used for the determination of the density of small solids without having recourse to balances. The author's instrument, however, differs by being designed to measure not the densities of the small submerged soil particles but merely their submerged weight. The accuracy of the author's pouch-hydrometer is the same as that of the Nicholson hydrometer and depends essentially on the thickness of the hydrometer stem. Stems having a cross-section as small as 0.5 square millimeter are practicable, corresponding to a weighing—accuracy of 1 mg. *i.e.*, 0.1 % of a one-gram sample of soil or an accuracy of 1 % approximate when measuring suspended material in a 1/10 aliquot part of a suspension containing a one-gram soil sample. This is many times better than the discrepancies encountered quite usually—especially with local soils—between results obtained by common hydrometer methods and the pipette method. The stem, on the thinness and uniformity of which accuracy depends most, is best made from fine glass-rod or alkali-resistant plastic or stainless steel and inserted into the stem hole of the hydrometer bulb, plugging it hermetically. A scale is later engraved on it and the whole stem covered thinly and evenly with a water repellent.

The bulb and the pouch contained therein as seen in the illustrations, are best blown of glass. Pouch volume is between 30 and 40 c. c. If the

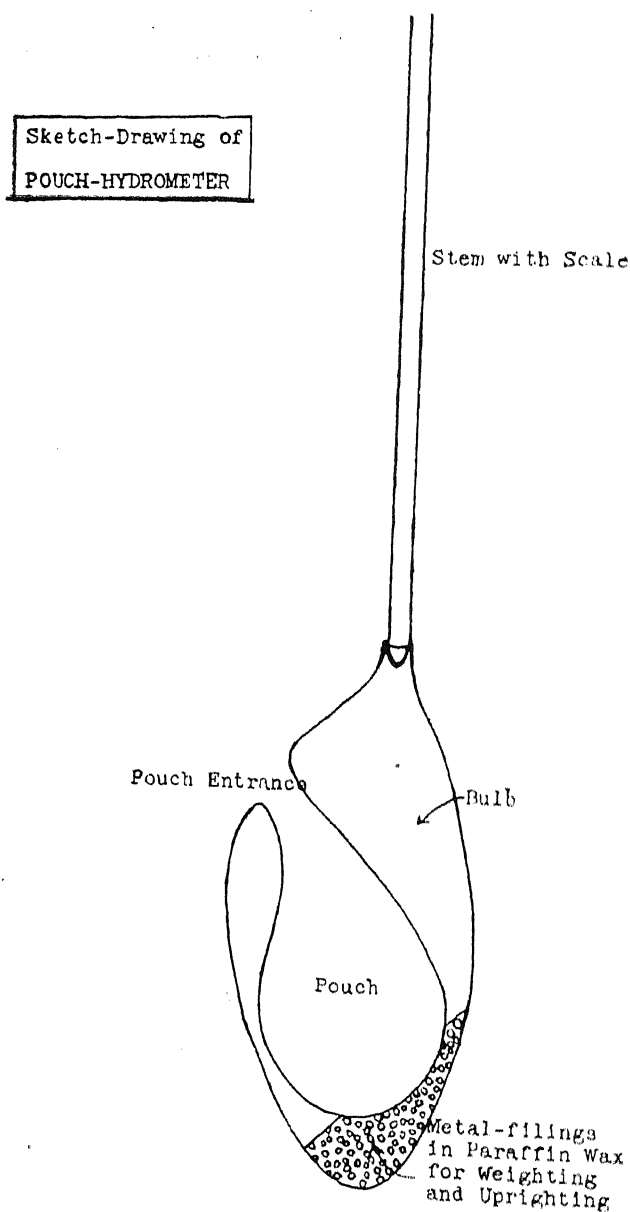


Fig. 2

bulb and pouch are very carefully shaped it will be easy thereafter to weight the hydrometer for upright floating: the needed amount of tara is introduced into the stem hole in the form of mercury and the hole sealed. But if this fails to ensure upright floating position of the hydrometer, fine metal filings mixed with paraffin wax may be used instead of mercury, tapped into such a position

within the bulb which by trial is found to force the floating hydrometer into upright position and caked permanently into this position by slightly warming and re-cooling the bulb. Just enough taring material is introduced during this operation to make the scale of the hydrometer read zero when the instrument is floating in clear soil dispersion solution with nothing but this liquid in its pouch. Care must always be taken when inserting the hydrometer into a liquid that this liquid enters the pouch and fills it completely so that no air bubbles remain anywhere in it or adhere externally to the hydrometer bulb.

The grading of the hydrometer's scale can be done in such a way as to render direct readings of percentages when carrying out routine analyses: The exact amount of soil used for each analysis—say one gram or more—is dispersed and the usual aliquot portion of the stirred-up suspension (25 c. c.) pipetted into the hydrometer pouch. Taking care as before to have all the remaining air in the pouch expelled on immersion, the thus loaded hydrometer is floated again in the previously used clear soil dispersion solution. The reading this time gives the upper end—100%—of the scale, which then is proportionally subdivided. It is the essence of this mode of hydrometer use that no motions whatsoever of the soil particles within the suspension can bias the reading of the hydrometer. (This is true, of course, only as long as the operator avoids creating so strong turbulence in the clear external liquid that could pull the soil particles out through the pouch-entrance).

#### MODE OF OPERATION :

A soil suspension is prepared as prescribed by the original pipette method or according to one of its newer versions employing modern dispersing agents, and permitted to sedimentate. As in the pipette method, after prescribed time intervals samples of the suspensions are drawn from a given depth in the column by means of a pipette (25 c. c.). From the pipette these samples are now released into the pouch of the hydrometer which is then floated with the familiar precautions in the clear soil dispersion solution. If the same conditions as during calibration (see above) have been observed the hydrometer reading indicates directly the amount of material suspended in the pipetted volume, expressed in percentages of the total. Generally, the amount of suspended material contained in the hydrometer pouch can be calculated from the observed dip of the hydrometer scale by the formula

$$D_w - D_o = \frac{W + V(S_m - S_o)}{r^2 \pi S_o}$$

where  $D_o$  and  $D_w$  stand for the dip of the hydrometer stem with pouch empty\* and loaded, respectively,

$W$  is the submerged weight of the suspended soil inside the pouch,

$v$  is this volume of suspension pipetted into the pouch,

$S_o$  and  $S_m$  are the densities of the clear dispersion solution and the actual suspension medium, \*\*) respectively,

and  $r$  is half the diameter of the hydrometer stem.

As seen from the foregoing, results obtained by the gravimetric version of the pipette method and results obtained by the described pipette-hydrometer combina-

\* *i. e.*, containing only clear solution.

\*\* If a suspension medium different from that used during calibration is employed.



tion method of necessity must be identical. This is indeed always found to be the case. Differences could be theoretically possible only for soils the mechanical fractions of which would differ extremely with respect to their true densities, since in the gravimetric version the dry-weight percentage relationship between the various fractions are determined, whereas in the combination method submerged-weight percentages are determined. The differences of true density between the mechanical soil fractions in normal soils are much too small to make themselves felt by causing discrepancies between the two versions of the pipette method, the one using balances and drying equipment, the other one—described here—wet-weighing by means of the pouch hydrometer.

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## HARDENING OF CLAY

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The soil is essentially a disperse system, in which the dispersed or soil phase consists of particles of varying size fractions ranging from colloidal state to the coarser ones. The colloidal behaviour of very fine soil particles makes the interaction between the solid and the liquid constituents sufficiently complex. Terzaghi<sup>2</sup> has reported that "if a sample of a very fine soil fraction is thoroughly disturbed, it acquires cohesive strength, first at a fairly rapid rate and then more and more slowly. If the sample is again kneaded at unaltered water content, its cohesion decreases considerably, but, if it is once more allowed to stand, its cohesion is completely regained. This phenomenon is known as thixotropy, the softening and subsequent recovery seem to be due to the destruction and subsequent rehabilitation of the molecular structure of the absorbed layers." A Casagrande<sup>3</sup> pointed out that the consolidation characteristics of undisturbed and remoulded clays differed greatly. It was also observed that at given pressure the void ratio of the undisturbed sample exhibited higher value.<sup>1</sup> During the investigation of land slides, the Swedish Geotechnical Commission<sup>5</sup> experienced the above phenomenon of decrease in strength of clays on remoulding at the same density and moisture content.

Remoulding is considered to break down the highly complex structure of the original material. The earlier scientists did not realise its importance, that when soil is removed from a bore hole, something happens to it. Oreste Moretto<sup>4</sup> concluded that the remoulded soils began to regain their lost strength when placed for a certain period of time at an unaltered moisture content. These observations have great effect upon the stability of the embankments and other allied engineering works. In view of the great practical importance of this phenomenon, a detailed study was carried out in order to examine the validity of the above observations and to investigate its cause.

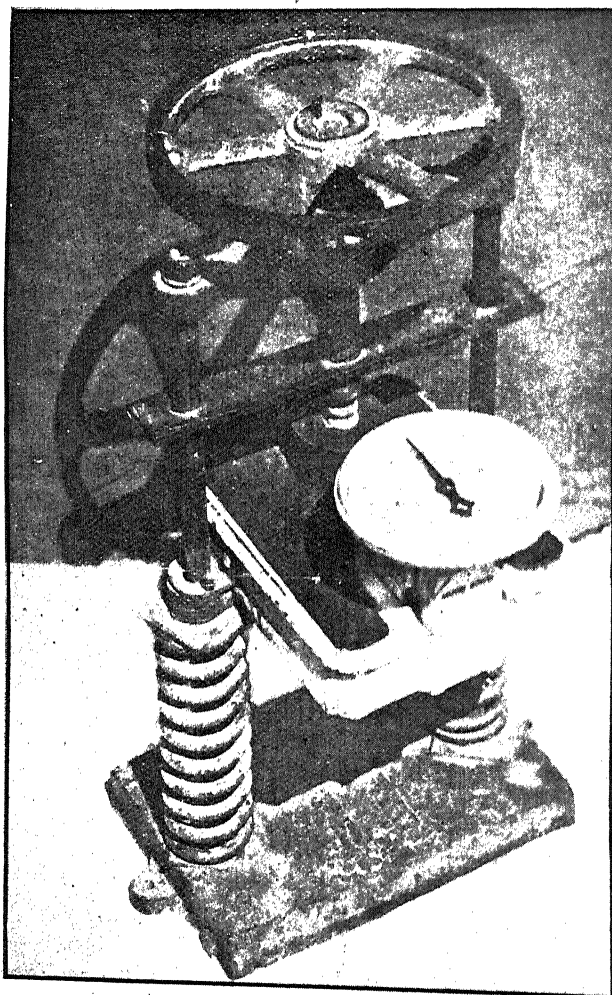
### EXPERIMENTAL

The following experiments were carried out :—

1. The first experiment sought to determine the compressive strength and slaking of undisturbed and remoulded soils compacted at the same natural density and moisture content, both in the wet and dry conditions. One inch cube soil blocks were taken in both the cases.
2. The 2nd experiment related to the effect of age on the regain of compressive strength of compacted blocks at 1.6, 1.7, and 1.8 dry bulk densities and at

8.0%, 10.0%, 12.0%, 14.0%, and 16.0% moisture content. The soil blocks were kept in sealed jars containing soils of the same moisture content at which the blocks were compacted. An average value of the compressive strength of five blocks was taken at every time. The compressive strength of soil blocks was determined by the cohesion machine (plate 1). The slaking time was found out by noting the time taken by the complete disintegration of the soil blocks placed on a wire gauze in water (Fig. 1).

Plate 1

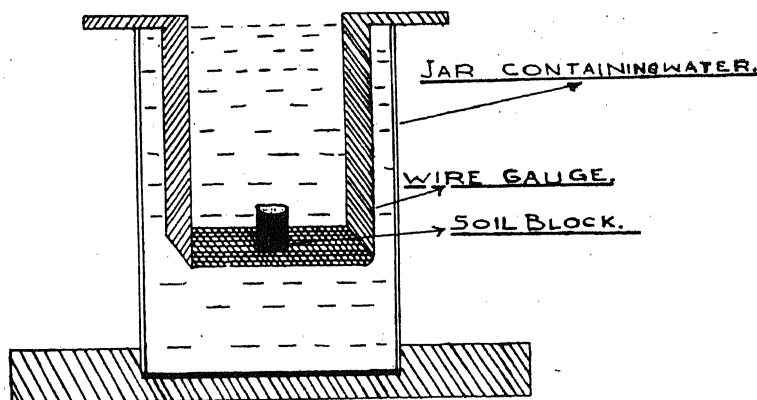


COHESION MACHINE.

The compressive strength and the moisture content of the soil blocks kept at varying moisture contents in sealed jars were determined after one day, one week, one month, three months, six months, and one year curing.

Fig I

An apparatus for the determination of slaking of soils.



The mechanical analysis of the soil used in the second experiment was as follows :

Clay (Particles below 0.002 m.m.) = 17.6 %

Silt (Particles greater than 0.002 m.m. but less than 0.02 m.m.) = 18.1 %

Sand (Particles greater than 0.02 m.m. but less than 2.0 m.m.) = 64.9 %

pH = 8.0

The soil was predominantly kaolinite.

#### DISCUSSION OF RESULTS

A perusal of the results showed that the compressive strength and slaking time of undisturbed soil samples (both in the wet and dry conditions) were greater than the remoulded samples (Table I). Secondly the remoulded samples regained strength even up to one year curing (Table II). The moisture content practically remained constant even after one year curing.

TABLE I  
HARDENING OF CLAY  
COMPARATIVE COMPRESSIVE STRENGTH AND SLAKING TIME OF  
UNDISTURBED AND DISTURBED SOIL SAMPLES

Sr. No.	Moisture %	Dry Bulk Density in Grms/cc.	Undisturbed Samples Compressive strength in Pounds/Sq. inch		Time of Disinteg- ration in Seconds		Remoulded Samples Compressive Strength in Pounds/Sq. inch		Remoulded Samples At same Moisture and Density Time of Disintegration in Seconds	
			WET	DRY	WET	DRY	WET	DRY	WET	DRY
1	2.8	1.72	113.2	200.4	47.4	42.4	128.2	60.8	95.4	14.8
2	3.8	1.63	114.2	154.6	39.4	46.4	3.4	51.2	58.2	39.2
3	7.15	1.7	27.4	...	...	74.5	6.6	...	22.8	12.8
4	7.35	1.84	61.85	...	53.25	62.5	15.4	...	13.3	11.8
5	8.0	1.67	11.0	136.0	1099.0	236.0	11.0	126.0	1080.0	225.0
6	8.2	1.49	8.0	105.6	115.2	138.0	10.0	36.2	31.0	22.0
7	10.1	1.78	19.75	174.2	289.0	128.0	57.0	218.0	516.0	315.2
8	10.4	1.6	9.25	2020.0	...	...	9.4	155.6	...	...
9	12.0	1.83	14.0	158.0	1288.0	286.0	12.0	134.0	1092.0	225.0
10	15.0	1.62	12.0	70.0	600.0	89.0	10.0	63.0	599.0	68.0
11	16.0	1.62	20.0	136.0	1030.0	240.0	18.0	100.0	945.0	171.0
12	10.0	1.73	20.0	162.0	925.0	199.0	18.0	125.0	809.0	176.0
13	16.3	1.36	14.6	224.4	...	...	9.3	180.6	...	...
14	18.0	1.59	14.0	70.0	570.0	120.0	6.0	60.0	540.0	95.0
15	18.0	1.62	11.0	128.0	1080.0	223.0	11.0	118.0	1020.0	210.0
16	18.0	1.63	12.0	66.0	620.0	100.0	10.0	70.0	599.0	78.0
17	18.0	1.66	11.0	146.0	1140.0	240.0	10.0	129.0	1080.0	225.0
18	18.0	1.67	22.0	113.0	9110.0	129.0	16.0	100.0	839.0	120.0
19	18.0	1.70	22.0	140.0	1128.0	190.0	16.0	130.0	956.0	175.0
20	19.0	1.61	16.0	90.0	620.0	119.0	8.0	78.0	565.0	105.0
21	19.0	1.63	18.0	111.0	875.0	165.0	14.0	104.0	836.0	149.0
22	20.0	1.66	14.0	20.0	765.0	80.0	10.0	78.0	605.0	60.0
23	20.0	1.67	10.0	88.0	640.0	60.0	10.0	88.0	585.0	60.0
24	20.0	1.77	13.0	91.0	560.0	70.0	13.0	88.0	560.0	60.0
25	21.0	1.60	14.0	88.0	715.0	190.0	4.0	62.0	600.0	120.0
26	21.0	1.7	12.0	146.0	1165.0	236.0	11.0	143.0	1055.0	225.0
27	22.0	1.61	20.0	112.0	900.0	180.0	15.0	109.0	836.0	149.0
28	22.0	1.70	14.0	100.0	1060.0	120.0	14.0	90.0	920.0	80.0
29	22.0	1.74	12.0	148.0	1140.0	136.0	12.0	139.0	106.5	180.0
30										

TABLE II

EFFECT OF AGE ON THE REGAIN OF COMPRESSIVE STRENGTH

OF SOILS BLOCKS COMPACTED AT VARYING DENSITIES AND

MOISTURE CONTENT

		COMPRESSIVE STRENGTH IN LBS PER SQUARE INCH					
No	Moisture of Compaction (mean value)	Moisture at the time of testing	VARYING PERIODS OF CURING				1 Year
			24 Hours Density	1 Week of	1 Month Compaction	3 Months 1.6 (D. B. D.)	6 Months
1	8.0 %	8.1 %	12.0	13.0	14.0	17.0	21.0
2	10.0 %	9.8 %	15.0	15.0	18.0	25.0	35.0
3	12.0 %	12.0 %	19.0	23.0	15.0	28.0	35.0
4	14.0 %	13.7 %	17.0	19.5	21.0	24.0	26.0
5	16.0 %	15.7 %	6.0	6.5	8.0	11.5	15.3
							19.0
DENSITY OF COMPACTION 1.7 (D. B. D.)							
6	8.0 %	8.0 %	13.0	15.5	16.0	25.0	40.8
7	10.0 %	9.7 %	14.5	18.0	13.0	28.0	42.5
8	12.0 %	12.2 %	18.0	27.0	31.0	38.0	43.0
9	14.0 %	14.1 %	14.0	17.0	20.0	25.0	35.0
10	16.0 %	15.84 %	9.0	10.0	13.0	27.0	23.0
							29.0
DENSITY OF COMPACTION 1.8 (D. B. D.)							
11	8.0 %	7.9 %	15.0	21.0	26.0	29.0	63.0
12	10.0 %	9.8 %	20.0	23.0	36.0	47.0	69.0
13	12.0 %	12.1 %	28.0	33.0	45.0	41.0	79.0
14	14.0 %	14.0 %	27.0	30.0	43.0	47.0	56.0
15	16.0 %	16.0 %	24.0	27.0	32.0	33.0	48.0

It was very interesting to observe that the compressive strength of all the soil blocks was maximum in the case of blocks compacted at moisture content between 10.0 % and 12.0 %, the optimum moisture content being 11.65 %. It means that this moisture content allowed the compactive force to arrange the fines efficiently into the voids of the correspondingly larger grains and resulted in maximum strength. For every soil there is a special moisture content at which its density is maximum. This moisture is known as Optimum moisture content.

The question to be answered is "Why the undisturbed samples or those kept for a certain period of time at constant moisture content give greater compressive strength than the remoulded ones."

Terzaghi<sup>8</sup> is of the opinion that the strength and rigidity are acquired previously by "slow physico-chemical processes," which are due to the surface activity of the mineral grains. As a consequence of its surface activity, each clay particle is surrounded by a shell of particles and is quite viscous within a somewhat greater distance. During sedimentation, the mass of clay consolidates, the solid parts of the water shells may come into contact and merge at a number of points in the clay mass and, as a consequence, the mass becomes stiff. Remoulding breaks the contacts between the solid water shells, displaces the grains, and introduces viscous adsorbed water between them; where upon the clay becomes plastic. "A Casagrande<sup>3</sup> proposed a theory according to which the clay particles settle during the process of sedimentation into a definite arrangement called the clay structure. His conception of the structure is that of a coarse grained skeleton cemented together by highly compressed clay whose interstices are filled with soft clay." Casagrande further states that the building up of such a structure is chiefly dependent on the exceedingly slow process of natural sedimentation and consolidation.

The results of compressive strength and slaking time both in the wet and dry conditions (Table I) also indicated that remoulding could not arrange the different size particles in the manner formed by age in the case of undisturbed samples. Age has definitely produced a special pattern. The effect of time is, therefore, of great significance.<sup>9</sup> The results of slaking time also afforded an additional evidence to the above view point. The time of disintegration of the wet and dry blocks of remoulded soils, being comparatively less than the undisturbed one showed clearly the variability of the solid structure in the two cases.

Regarding the conception of thixotropic<sup>6</sup> phenomenon, this takes place in montmorillonite type of soils *i.e.*, Bentonite. The soils used for this study were of Kaolinite type. Therefore the question of thixotropy, being the dominant factor in increasing the compressive strength does not seem to hold good in this case.

In this connection the theory outlined by Barber<sup>2</sup> merits attention. He states that the distribution of moisture may have considerable effect on the strength. In Table II are presented the results of the compressive strength of soil blocks cured for varying periods. As stated under "experimental" these blocks were kept in jars containing soil of the same moisture content as that of the blocks. Therefore these blocks were not under any static or dynamic load which could produce any change in the structure during the period of observations *i.e.*, one year. But the results showed that there was a gradual increase in the compressive strength (Table II). This means that with time there was more uniform distribution of moisture around the solid particles, which gradually increased the compressive strength. It is a matter of common observation that the strength is always at its weak juncture. If the moisture film is not uniformly thick around the soil particles, which can be

possible in the case of freshly compacted blocks, this would naturally result in lower strength as compared with blocks which have been stored at constant moisture before testing due to the equalisation of the moisture film around the particles, with age. This factor contributed for the lower strength and lesser slaking time in the case of remoulded samples. On drying unequal stresses were produced due to the non-uniformity of the moisture film, hence lower strength and lesser slaking time were exhibited by the remoulded samples.

The above results have special significance in the construction of earth dams and embankments, as the bearing capacity of the compacted fills will increase gradually with age. This factor should be taken into consideration during the design of earth structures.

#### SUMMARY

- (i) The compressive strength and slaking time of the undisturbed soil samples are greater than the remoulded samples, compacted at the same natural density and moisture content.
- (ii) The compressive strength of the compacted samples increase gradually with age, sometimes more than 100.0%. The reason of the increase in compressive strength with age may be due to more uniformity of moisture film around the particles.
- (iii) The maximum increase in the compressive strength with age is observed in soil blocks compacted at the Optimum Moisture Content.
- (iv) The main reasons for the lower strength in the remoulded samples may be due to the non-uniformity of moisture films around the soil particles and the different particle arrangement from the natural pattern built with age.

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# A GENERAL REVIEW OF THE EFFECT OF DRYING ON SOIL PROPERTIES

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(Communicated by Dr. H. L. Nigam)

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The effect of drying on soil properties has been a subject of study for a very long time, Gustafson (1922) and Steenkamp (1928) besides others, having reviewed the work on this subject, almost two decades ago. The review in question referred to a period when soil science had not developed. During the last two decades, many of the old ideas have given place to new ones. New theories have been developed which incidentally make the old information very confusing and obsolete. An attempt has been made here to link the old and new ideas for a better understanding of the subject. For the convenience of discussion, the subject is dealt with under five different heads.

**THE EFFECT OF DRYING ON THE MICROBIAL POPULATION.** The changes in the biological make up of the soil consequent upon drying have been very extensively studied by investigators like Rahn (1907), Ritter (1907), Waksman and Starkey (1923), Allison (1917), Engberding (Waksman 1952).

Allison found that the soil changed biologically to a marked extent during storage in the laboratory. Compared to a fresh sample brought from the field, the sample stored for two hours in the winter season showed a definite decrease of 30 to 40 % in the bacterial count as a result of storage. However the effect on soil fungi was not so marked as on the other organisms. Lebedjantzev (1924) reports similar depressing effect of drying on the microbial population of the soil. Mortenson and Duley (1931) in their studies on a sandy loam soil found a lowering in the number of bacteria after sun-drying. The sun-dried sample showed 400,000 organisms per gm. of soil as against 5,450,000 in the fresh soil. There are other investigators like Engberding, who did not observe any difference in the bacterial count of fresh and dried samples. Some of Engberding's figures are reproduced below :—

Moisture content of the soil-% moisture	22.7	14.1	10.9	6.5
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Total bacteria in the soil thousands/gm.	25,280	16,410	11,890	9,980
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According to Khalil (Boken 1952) about 20 % of the bacteria were still alive in the soil after it had been air-dried to about 5% moisture content.

The increase in the electrical conductivity of aqueous suspension of soils, has been suggested by Asthosh Sen (1932) as an index of their fertility. This increase is caused as a result of enhanced bacterial activity which is responsible for making some of the inert soil constituent soluble. He found that air-drying increased the conductivity of soils.

**THE EFFECT OF DRYING ON THE SOIL CONSTITUENTS.** Gustafson (1922) studied the effect of drying soils on their water-soluble constituents. He observed that

air-drying brought about a marked increase in the total soluble salts in a water logged soil. The increase varied from 23% to 150 % in the two soils. The nature of these salts was not studied. Hall noticed a marked increase in total soluble salts in four soils dried for about 5 months. Coles and Morison (1930, 1932) observed a considerable increase in the amount of water soluble substances in an air-dried soil. They found an increase in the water soluble Ca, K and  $\text{PO}_4$ . Mortensen and Dulcy (1931) studied the effect of drying on the amount of water soluble calcium and found that it was doubled when the soil was air-dried in the sun. Whitney and Cameron (1903) studied four soils and observed that drying of the soil affected the solubility of  $\text{PO}_4$ ,  $\text{NO}_3$ , K, Ca and organic matter. Some of Whitney and Cameron's results are given below :—

SOIL	CONDITION	P. P. M. of oven dry soil			
		$\text{PO}_4$	$\text{NO}_3$	Ca	K
Black clay	Fresh	8.6	7.1	7.8	15.2
	Air-dried	9.6	8.5	12.7	21.9
Truck soil	Fresh	6.7	23.6	10.3	16.4
	Air-dried	10.4	30.2	15.5	20.4
Mount pleasant Soil	Fresh	9.1	2.3	20.6	11.2
	Air-dried	11.9	3.6	33.0	11.5

Wiklander and Hallgren (1949) who studied the effect of drying on the acetic acid soluble P in Gytta soils, found a pronounced decrease in the acetic acid soluble P in the sub-soil on drying.

These results are as under :—

Depth in inches	Soil pH	P extracted by 2.5% acetic acid mg. $\text{P}_2\text{O}_5$ /100 gm. dry soil	
		Undried	Dried
0-20	7.56	28	19
30-50	4.6	8.2	1.5
80-100	4.06	8.03	1.3
120-140	4.36	57	15
160-180	7.7	103	27
200-220	7.9	101	30

The above results refer to the soils which were under water-logged conditions. It is well-known that under such conditions iron in ferrous form is the prominent ion. On dehydration the ferrous iron gets oxidized to ferric state and as the latter has a stronger affinity for  $\text{PO}_4$ , it is more tightly adsorbed. Hence the difference in the level of acetic acid soluble P of the fresh and dried samples may be due to this chemical action.

Wiklander (1950) in his studies on a pedalfers soil of Kungsängen, found a considerable increase in  $\text{PO}_4$  retention by the soil as a result of drying, there being a decrease in the exchangeable  $\text{PO}_4$  as shown below :—

Soil	Surface	Sub-soil	P retained by the soil, mg. $\text{P}_2\text{O}_5$ /100 gm. soil.
Undried	234	278	
Dried	415	457	

Coming now to potassium as the third important plant nutrient, it is well-known that a part of the applied K is turned into a non-exchangeable form thus making it difficultly available to plants. Volk (1934), Page and Bayer (1939) Attoe

and Truog (1945) have shown that this fixation or unavailability of K is increased by alternate drying and wetting of soils. Stanford and Pierre (1946, 1947) have found illite to be effective in fixing K in the moist state when the pH of the clay system was high and that drying increased fixation of K by illite as well as montmorillonite. Attoe (1946) in his laboratory studies on the effect of alternate wetting and drying on the fixation and release of K in the soils, found an increase in the content of exchangeable K in nine out of ten soils. The actual increase varied from 4 to 90% over the moist soil. In soils fertilized with K, however, he found fixation of K in every case and 11.52 per cent. of the applied K was not recovered by cation exchange. Volk (1934) states that K changes to non-exchangeable form in part under conditions of alternate wetting and drying. This is characteristic of Montmorillonitic and illitic clays but not of kaolinitic clays. The change from exchangeable to non-exchangeable form is accompanied by a reduction in the total exchange capacity. According to Chatterjee (1953), the decrease in the recovery of K from fertilized soils is due to its entry into the crystal lattice to form a new mineral (hydrous mica), the K being entrapped between two sheets. Regarding the effect of drying on exchange equilibria in soils, Page and Bayer (1939) have noted that in the case of hydrogen saturated bentonite (beidellite), drying at 100°C reduced the replacement of hydrogen by various cations, and more particularly by K. Mattson (1929) noticed that swelling of K-saturated montmorillonite was greatly reduced by previous drying.

Steenkamp (1928) studied the effect of dehydration of soils upon their colloidal constituents. He used 3 soils, and found a large increase in the exchangeable cations and the increase was related to the degree of weathering of the soil and also to its degree of saturation. On the other hand, Cokes and Morison (1930-32) demonstrated that after the soils are dried, they contain a smaller quantity of exchangeable cations than the original moist soils. Waksman and Starkey (1923) and Lebedjantzeb noticed that drying caused an increase in the solubility of organic substances.

In the report on the analysis of paddy soils from a manurial trial in Indonesia, submitted to the 2nd meeting of the Working Party on Fertilizer (F. A. O. 1953, paper No. 37), it is indicated that large differences in the results were obtained with and without drying, particularly with regard to extractable P, ammoniacal nitrogen, manganese and iron.

The effect of drying on the availability of micro nutrients in soils has been investigated by various works.

Parks and others (1944) showed that drying caused a decrease in the recovery of boron in the soil. Olson (1947) found that drying of the soil after boron was added, increased the amount of boron fixed. This increase was greater in limed than in unlimed soils. Steenbjerg (as quoted by Leeper 1953) observed that if the soil is allowed to dry before extraction, it liberates less copper.

The content of exchangeable manganese in the soil depends on the state of hydration of the soil when extracted with an electrolyte. Many workers report that drying affects the level of exchangeable manganese in the soil.\*

Using molar magnesium nitrate as the extracting agent and leaching until the mole had passed through 100 gm. of soil, Boken (1952) finds an increase from 15 P. P. M. in fresh soil to 27 P. P. M. in the same soil after 6 weeks and to 35 P. P. M. after 6½ months of drying (soil pH 6.5). Kikuo Ishii (1951) who

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\* Steenbjerg (1933), Sherman and Harmer (1942), Fujimoto and Sherman (1946), Heintze (1946), Boken (1952), Zende (1954).

studied seven soils from the rice fields in Japan, noted that four out of seven soils showed a remarkable increase in the KCl-extractable manganese after air-drying. Zende (1954) studied the slow reduction of Mn oxides by the organic matter during the process of air-drying in ten different soils. From the results, he concluded that the effect of air-drying on the extractable manganese is seen most strongly in soils with pH less than about 6.3 and the effect is dependent on the amount of active manganese, the kind of organic matter and the nature of the oxide.

**EFFECT OF DRYING ON THE DEGREE OF AGGREGATION.**—Thorough drying of soils makes a clay more difficult to disperse as found by Steenkamp, Smolik (1927). The effects of drying on the structure (Downs and Leeper 1940), on the settling velocity of the colloidal material (Mortensen and Duley 1931) and on the reversibility of colloids (Beaumont) are all of the same nature.

**EFFECT OF DRYING ON SOIL pH.**—The effect of drying on soil pH has been studied by many workers. Haly and Karrakar (1922) observed that air-dried soil show a slightly greater H-ion concentration than moist soils. Rost and Fieger (1923) studied the effect of drying and storage upon the H-ion concentration on soil samples. Five soil samples from liming experiments showed considerable differences as a result of drying, the moist soils showing 0.03 to 1.17 units of pH higher than the air-dried soils. They also studied the effect of drying on soil pH in glacial and loessal soils and sub-soils.

Baver (1927) studied the nature of various factors affecting the H-ion concentration of soils. He observed a change in H-ion concentration of air-dried soils.

In acid soils the differences between dried and moist soils were not significant, but in alkaline soils, air-drying caused a considerable decrease in alkalinity.

Achrameiko (Loc. cit.) in U. S. S. R. studied the effect of drying on soil pH. He found that sun-drying made the soil slightly more acid. E. Boken (1952) observed a slight decrease in pH values of soil samples when they were stored (in air-dry state at 20°C). Burges (1922) studied the effect of drying on the H-ion concentration of soils. He found that air-drying in case of Miami silt loam had little or no effect on pH values of acid soils, but drying alkaline soils rendered them somewhat less alkaline.

Arrhenius (1922) and Bilman (1927) found no change in pH value, obtained by indicator method in alkaline soil, air-dried at 100°C. Steenbjerg (1933) remoistened an air-dry soil and then dried it again. He found no effect on the soil pH.

In the report of the first meeting of the Working Party on Fertilizers (F. A. O. 1951), it is stated that in Japan, when dry soils become water logged, considerable chemical changes take place. On water logging, the pH values increase and so does the exchange acidity. There are 3 principal reasons for the increase in pH values (a) reduction of ferric iron to ferrous iron, which is a stronger base, (b) increase of ammonia, (c) reduction of sulphuric acid to hydrogen sulphide, a weaker acid. The increase of exchange acidity is accounted for merely by the increase of ferrous iron in the exchange complex.

An increase in the H-ion concentration after drying has also been observed by Zende in his studies on Australian soils. (Un published). The exact cause for such decrease in pH is so far not investigated. However, the observation of a few workers suggest the following possibility of decrease in soil pH after drying :—

(a) *Changes in the colloidal equilibrium.*—When the soils are air-dried for a long time, they take more time to come to equilibrium after remoisturing, due to the irreversibility of colloidal material.

(b) *Dilution effect.*—Perkins and King (1931) have shown that if the moisture in the soil is not taken into consideration, measurement of pH of a moist soil shows higher values than the air-dry soil. They consider this as a dilution effect.

(c) Entry of some cations in the clay lattice on drying and thereby becoming non-exchangeable and the difference in the degree of hydration of these cations may reflect on the equilibrium of cations and thereby may effect the pH of the soil suspension.

THE EFFECT OF AIR-DRYING OF THE SOIL BEFORE FLOODING.—E. J. Russel (1950) referred to the beneficial effects of soil drying on crop production. He and subsequent workers attributed this effect to a kind of partial sterilization when soils are treated with volatile antiseptics such as toluene. The beneficial effects of drying wet paddy soils on rice production have been known in Japan for a long time. The effect of soil drying prior to flooding on the accumulation of ammonium nitrogen after flooding is distinctly established in the laboratory experiments. According to Shingo Mitsu (1952) air-drying of soil prior to flooding not only increased the available nitrogen, but also the available  $P_2O_5$ . These experiments were carried at Agricultural Experimental Station, Nishigahara, Tokyo-Japan.

The air-drying of the soil gives rise to an increase in easily decomposable organic matter and this in turn results in a more reduced soil condition after flooding. He further states that the rise in pH of the air-dried soil as compared to the non-dried soils under flooded condition, will be one more reason in increasing the solubility of phosphoric acid as it possibly accelerates the hydrolysis of ferrous phosphate, replacing  $P_2O_5$  combined with ferrous iron with hydroxyl ions.

From the above review of work, carried out by various investigators, it is important to note that air-drying of soils brings about considerable changes in their physico-chemical and biological properties. In view of these changes, the normal practice of storing and drying the soils before analysis, needs to be examined very critically.

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# HYSTERESIS IN MOISTURE CONTENT—SUCTION RELATIONSHIPS IN SOILS

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In soil moisture studies, the phenomenon of Hysteresis in soil moisture characteristics is of significance both theoretically and practically. For the purposes of this discussion, moisture characteristics from two dissimilar materials are shown in Figs. 1 and 2.

The experimental procedures involved have been recently described (Collis-George 1955) and it will suffice here to state that the non-swelling system of sintered glass was examined on a tension-plate apparatus, whilst the swelling clay results were obtained by tension plate, pressure membrane and vapour pressure techniques. The non-swelling constant structured material of Fig. 1, was made by sintering 15 gm.  $\frac{1}{4}$ — $\frac{1}{2}$  mm. diameter pyrex beads in a mould of the dimensions of the tension plate equipment. The swelling material of Fig. 2, was a clay separate less than one micron in equivalent settling diameter, of a Na-Montmorillonite from Belle Fourche, South Dakota. The clay dispersed in distilled water was concentrated by settling under gravity, and by slight suction, on the pump to form a gel of moisture content 1500 per cent. oven dry weight and of approximately zero suction since the gel stood in the presence of excess water without expansion.

The experimental procedures were such as to allow both desorption and wetting relationships to be obtained on both materials. The datum of moisture content was oven-drying at 105°C until constant weight was reached. This heat treatment of the clay, which was powdered by gentle crushing before adsorption experiments, might perhaps have altered the internal micellar structure relative to that in the drying gel. This dry clay (less than 200 mesh) by inspection obviously contained aggregates, which as they were wetted produced a swollen oolitic mass. Thus the wetting and drying clays are different in this structural sense, at least, but on complete relaxation of suction, the wetted gel was only distinguishable from the initial gel by this macro-structure which was mechanically unstable; and hence it is presumed, in this discussion, that the differences between the clay wetting and drying as caused by oven drying and crushing are restricted to a macro-structural effect, which could be expected to influence the moisture characteristic by an increase of about 30 per cent. moisture content, only at the lower suction values as compared with a total moisture content of 1500 per cent.

The removal of moisture in a constant structured material can only be by pore emptying and air entry, where the radius of neck of the pore controls the

suction necessary for the air liquid interface to penetrate the cell. In pore filling of a constant structured material, it has been suggested (Haines, 1930) that the

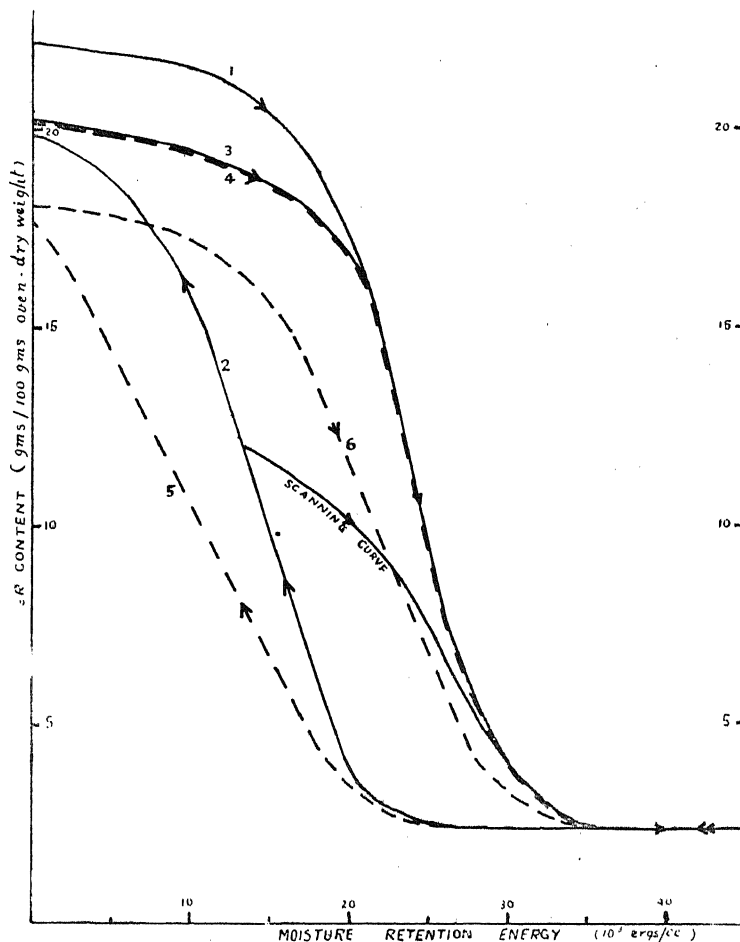


Fig. 1, Moisture characteristics of a sintered disc composed of  $\frac{1}{8}$ — $\frac{1}{4}$  mm. pyrex beads, at 25°C. Solid lines are for air-water interface and broken lines for benzene water interface. The moisture retention energies for benzene-water interface have been adjusted to those for air-water by the ratio of the interfacial tensions. The sequence of operations to produce these results :

- (1) pore emptying from water saturated condition by curve 1 ;
- (2) pore refilling and air entrapping by curve 2 ;
- (3) pore emptying and air entry by curve 3 ;
- curves 2 and 3 forming a reproducible cycle for the air-water interface ;
- (4) refilling again by curve 2 ;
- (5) a layer of benzene now put on the wet disc and on water removal benzene enters the system by curve 4 ;
- (6) displacement of benzene by water with some entrapping by curve 5 ;
- (7) removal of water and entry of benzene by curve 6 ;
- curves 5 and 6 forming a reproducible cycle for benzene-water interface.



radius of the pore is dominant. For ideal soils, to which the material in Fig. 1, corresponds, the ratio of pore emptying pressure/pore filling pressure is calculable and constant for all pores. If this hypothesis is correct, the replacement of the air-water interface by another of different interfacial tension should not alter the ratio of emptying/filling pressures, and only alter the absolute pressures by the ratio of the interfacial tensions, *viz.* 71.79 dynes/cm for air-water and 34.97 for benzene-water should alter the absolute pressures by the factor 2.06 at 25°C.

In Fig. 1, the benzene-water pressures have been adjusted to allow for interfacial tension so that the water-air and water-benzene relationships are directly comparable. A complication in such hysteresis experiments is that repetitively reproducible closed cycles as curves 2+3, and 5+6, are only obtained after a volume of air for 2+3, and air and benzene for 5+6, is entrapped in the porous system. It is interesting to note that the mechanism of entry of benzene-water

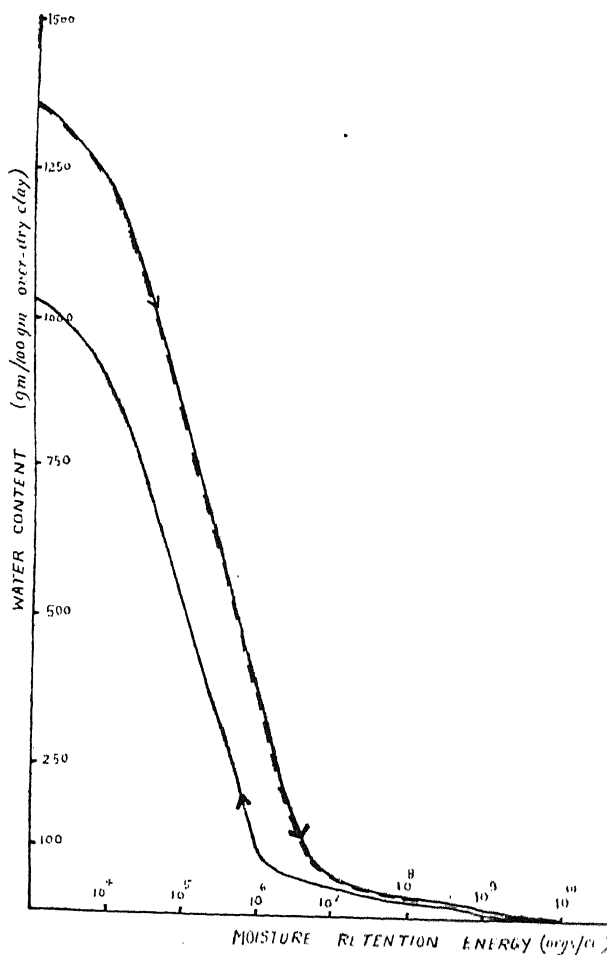


Fig. 2. Moisture characteristics for Na-montmorillonite (Belle Fourche) in equilibrium with distilled water. Broken line is for the system in the presence of benzene which did not penetrate the gel at pressures as high as 150 atmospheres.

is identical with air-water, as comparing curves 3 and 4, when benzene is first introduced into the system. Subsequently all pore emptying sequences follow a different relationship. The wetting-up curves for the two interfaces are always distinct. Examination of the emptying/filling pressure ratio for each interface shows not only a lack of constancy throughout each pressure range but also between interface; the ratio changing more rapidly with decreasing pressure for benzene-water than the air-water interface. Apparently therefore hysteresis is not completely controlled by the ratio of the pore and pore-neck dimensions, and the properties of the interface are of greater significance than merely its interfacial tension.

Fig. 1, shows that the drainage mechanism of water and its replacement by air or benzene is unique so long as the sample has not been previously wetted with benzene. After benzene treatment, less work is required to fill or empty pores with the apparent effect of an increase of pore-radii in this constant structured system. A constant amount of water remains in the mass after benzene or air entry and hence all pores, necks and surfaces must have identical film thicknesses of water and hence identical dimensions whether benzene or water is present.

A possible variable in this constant pore system is that of variation of angle of contact, but if the results of Fig. 1, are to be so explained it becomes necessary to have four contact angles. This multiplicity of values of the angle of contact, although surprising, would not be exceptionable, on the basis of a multimolecular adsorption theory of contact angle (Cassie, 1948). This would suggest, for the solid surfaces encountered in soils, that there are two types of sites in the case of the air-water interface, some sites being water wet and having zero angle of contact and others being air dry, having a finite angle of contact. The advancing water front would therefore have some mean finite angle of contact, whilst the front retiring from a wetted surface would have zero (or a very small) angle of contact. This hypothesis, to be valid, requires the ratio of dry to wetted molecular sites to remain constant, for the advancing front to obtain the characteristically reproducible hysteresis cycles, which are obtained regardless of the time taken in experimentation. In Cassie's experience with wool fibres, this requirement is always satisfied, but surprisingly, when compared with soil experiments, the draining characteristics for wool is not so reproducible. This explanation of hysteresis requires the surfaces of soil particles in general, and of glass beads in Fig. 1 in particular, to have adjacent molecular sites so markedly different in properties that in a water saturated atmosphere (just in front of the advancing water front) some sites remain dry and others wet, bearing in mind that these dry sites may have been wet very recently for the retiring front.

An independent proof that adjacent sites on the oxygen-hydroxyl surfaces associated with soil minerals have different water absorbing energies, is required before the contribution of a surface structure—angle of contact theory to hysteresis can be completely substantiated. This theory, however, easily explains the difference between the benzene-water and air-water hysteresis cycles, and more particularly explains why the advancing benzene front into a water-saturated zone has a different pressure relationship to the benzene front advancing into a water-saturated zone which has a previous benzene wetting history, on the basis of different ratios of water wet, benzene wet and air dry sites.

Fig. 1 shows for the air-water cycle, which is approximately parallel-sided, that the maximum difference in suction, which can be maintained at a constant

moisture content, hereafter called the hysteresis potential at a given moisture content, varies between  $9.5$  and  $11.5 \times 10^3$  ergs/gm over 90 per cent. of the moisture range while for benzene-water over the same range the potential varies from  $9.5$  to  $12.0 \times 10^3$  ergs/gm (corrected for interfacial tension). By graphical integration the cycles of hysteresis have total energies per 100 gm. of dry matter of  $8.3 \times 10^3$  ergs/gm (for 19.9 gm water) and  $9.3 \times 10^3$  ergs/gm. (for 17.7 gm water) for air-water and benzene-water respectively.

This numerical information, in the light of the previous discussion, would tend to suggest for rigid structures, that the geometry of the pore system is responsible for the majority of the hysteresis effect, and the contact angle theory, if valid, for about 6 per cent. of the phenomenon.

The results in Fig. 2, for a swelling clay show that the hysteresis phenomenon is of quite a different nature to that for the constant structured material. In the first place, the values of hysteresis potential vary from  $7 \times 10^9$  ergs/gm at 2 per cent. moisture content to  $5 \times 10^4$  ergs/gm at 1000 per cent. moisture content and the cycle of hysteresis has a total energy per 100 gm dry clay, of  $1.9 \times 10^7$  ergs/gm (for 1500 gm. water) for the air-water interface. Secondly the mechanism of water loss down to 36 per cent. water (at a suction of  $1.3 \times 10^8$  ergs/gm) is by removal of water from between platelets and micelles by shrinkage and not by air-entry, (see Collis-George, 1955, for a complete description of a proposed dehydration process). This is confirmed by use of benzene-water and air-water systems, when it is found that at the highest experimentally obtainable pressure in the pressure membrane equipment (150 atmos;  $1.5 \times 10^8$  ergs/gm) neither air or benzene penetration occurred, and up to this pressure the results for drying clay in the presence of air or benzene were identical, no interfacial correction being required. In this range of moisture contents, hysteresis cannot possibly be attributed to a pore dimension theory (Haines) and/or to a contact angle theory (Classie) as there is no interface inside the clay mass. Moisture hysteresis in these circumstances can only be attributed to a hysteresis in the interaction mechanism between micelles. Until the nature of forces involved in clay gels is more completely understood, e.g., the work of Schofield and Sampson, 1954, on Kaolin gels, it will not be profitable to continue the discussion of this type of hysteresis.

A recent general approach to hysteresis (Everett *et al.* 1952, 1954a, 1954b) is useful in explaining the shape and energies of hysteresis relationships, and in particular the shapes of the partial scanning curves within the main hysteresis envelope and their dependence on the previous history of the sample; such that in the case of soils, starting with a sample at a given moisture content and suction, it is not generally possible to predict the new moisture content-pressure relationships on changing the pressure, unless the previous wetting history is known. In this author's opinion, the hysteresis phenomena in soil-water relationships observed by numerous workers would self-evidently obey all the theorems proposed by Everett (1954a) and exhibit the phenomena required of his general hysteresis system. Unfortunately, however, as in any thermodynamical theory it is not possible to specify the mechanisms responsible for causing the phenomenon which obeys the thermodynamical treatment, so it is not possible to specify what causes soil-water hysteresis to obey the requirements of Everett's independent domain model of hysteresis. An independent domain here has the significance that at any particular pore, surface or neck of a pore it is possible for a group of water molecules to exist in two or more states, separated from one another by discrete energy intervals.

The results described are confined to the outer envelopes of the hysteresis cycle, where the previous history is precise and it is unnecessary to invoke much of the above treatment ; in Fig. 1, a typical scanning curve is included for completeness.

In conclusion, it would appear that at least one mechanism is required to cause hysteresis moisture-energy relationships in a swelling clay and two other mechanisms in rigid porous systems, and therefore at least three mechanisms in ordinary soils, and that the independent domain model of hysteresis, whilst aiding in the description of events, does not help us to decide which mechanisms are responsible. The contact angle theory of hysteresis in rigid structures is considered to produce about 6 per cent. of the phenomenon in comparison to the majority being caused by the geometry of the pores, on the experimental results discussed.

The majority of the experimental work here reported was made possible by facilities made available by the Department of Soils, University of California, Berkeley, to whom the author makes very grateful acknowledgment.

#### SUMMARY

Two markedly different materials, a constant structure of sintered glass and a colloidal Na-montmorillonite are compared from the aspects of their hysteresis moisture-energy relationships for wetting and drying. The evidence is in favour of, but requires independent substantiation of a variable angle of contact theory contributing about 6 per cent. to the hysteresis phenomenon for pores that empty and refill, the major part of the phenomenon being due to the geometry of the system. In non-emptying pores, which can expand or contract, the contact angle theory and the geometrical theory of Haines are inapplicable, and some further explanation, based on the interaction of colloidal particles is required. It is concluded that at least three mechanisms of hysteresis must be concerned in ordinary soils, and that whatever mechanisms are proposed must satisfy the independent domain model of hysteresis put forward by Everett.

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# THE PHYSICAL ASPECTS OF SOME CONCEPTS IN SOIL MECHANICS

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## I. INTRODUCTION

There is much common ground covered by the soil physicist and the engineer who is concerned with soil properties. The latter includes the oil field technologist, who is concerned with the flow of oil, gas and water to wells, just as the soil physicist is concerned with the flow of water to drains; and the foundation engineer, who is concerned with the reaction of soil to static loads, just as the soil physicist deals with the response of soil to loads applied by moving tillage implements. In particular, it seems inevitable that an application of soil mechanical techniques must ultimately lead to an objective assessment of soil texture which will be far more acceptable than the current empirical correlation between texture and mechanical composition, since soil mechanical properties are just those which enter into the cultivator's subjective assessment of texture. On the other hand it must be confessed that concepts and definitions in soil mechanics sometimes take for granted some naively oversimplified physical concepts, leading to puzzling inconsistencies. Here the soil physicist can perform a return service by indicating where further thought is needed and, if possible, by making some contribution to the analysis of the physical problem. It is the purpose of this paper to draw attention to the difficulties which arise when one attempts to discuss pore water pressure in clays which are subjected to a mechanical load, basing one's analysis on the assumption that the pore water must support the whole load since the clay particles are not in contact with each other. This discussion is of importance both in foundation engineering and in agriculture, since the overburden load may be shown to be a factor in determining the soil moisture profile (Croncy and Coleman, 1953).

## II. SOME ACCEPTED SOIL MOISTURE PHENOMENA AND DEFINITIONS

In agricultural discussions the soil is rarely considered as a medium subjected to compressive loads, since questions of the support of concentrated loads do not often arise, and great depths at which soil overburden pressure is a substantial factor do not often enter into problems. In such circumstances the moisture content of soil depends only upon the soil type and, for a given soil type, upon the suction experienced by the soil water. The soil water suction is commonly measured by means of a tensiometer, which is, in effect, a manometer which makes contact with the soil pore space *via* a fine-apertured porous membrane such as sintered glass, unglazed earthenware, cellophane or synthetic sausage casing. What is in fact being measured is the suction which must be



to destruction under compression, for each test will give a different pair of values of restraint and load, such as  $R$  and  $L$ , and  $R_1$  and  $L_1$ , and each such pair enables us to draw a different circle. Since each circle is known to touch the soil line, the latter may be drawn in as the envelope of the circles.

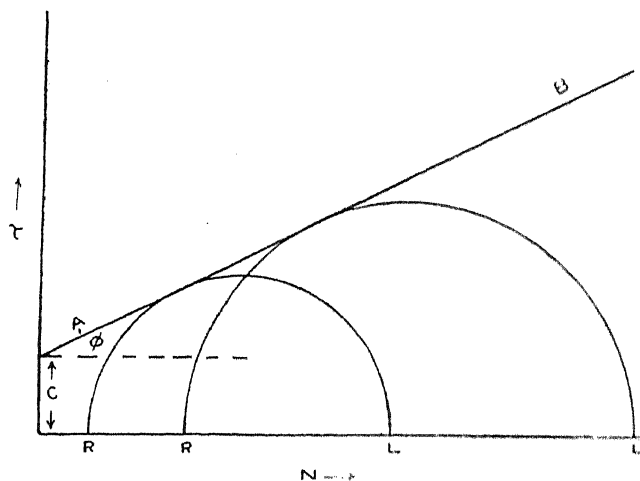


Fig. 1 Mohr's circles, and the relationship between the shear strength and normal load in soils.

### III. THE EQUIVALENCE OF SOIL WATER SUCTION AND UNIFORMLY APPLIED EXTERNAL PRESSURE

The analysis of the collapse of a soil column under load shows that the function of the restraint  $R$  is to press together the soil on the two sides of a plane along which failure is to take place, thereby necessitating a greater shear stress for failure, and at the same time to introduce a component of shear stress opposing that due to the destructive load  $L$ . The pressure  $R$  is usually applied hydraulically or pneumatically, and its purpose will clearly not be achieved if the pressure is transmitted also to the pore space. Since the outer space and the pore space are ordinarily continuous, an artificial barrier, such as a thin rubber membrane, must be interposed if the restraint  $R$  is applied hydraulically to a saturated soil, or pneumatically to an air-saturated sand; but if  $R$  is applied pneumatically to a water-saturated soil and is not of sufficient magnitude to force air into the pore space, the air-water interface will provide its own barrier. Air pressure may be applied in this way in a pressure plate apparatus (Richards, 1949), the internal pore pressure being maintained at that of the atmosphere by drainage of the soil through the permeable floor. The pressure difference  $R$  may clearly be applied by the alternative means of permitting the external pressure to remain at the ordinary atmospheric value and applying suction  $R$  to the soil water. This alternative procedure would seem to result in both moisture content and mechanical equilibrium remaining unchanged, and an experiment with sand to demonstrate this gave results which are shown in Fig. (2). A column of sand was erected on the flat platform of a sintered glass filter funnel, which was connected to a flexible U-tube and filled to the under side of the platform with water. Thus a measurable suction could be transmitted to the pore water in the

sand column. The sand was at all times saturated, this requirement limiting the suction to a maximum of about 10 cms. of water. The column was loaded, and the suction was then relaxed until the column collapsed, the experiment being repeated with different loads. Assuming that the suction was a measure of the lateral restraint, and that the sum of the suction and the applied load, together with the "overburden", was a measure of the destructive load  $L$ , the Mohr's circles and their envelope were drawn. The result shown is typical of triaxial compression tests of sand obtained in the usual way. A sand sample, represented by the point  $X$ , having an unknown suction  $s$ , would have a shear strength of appreciable magnitude  $C$  in the absence of an applied normal load, and  $C$  would represent the apparent cohesion of the sample. This effect is quite certainly a factor in the high values of cohesion observed in clays in field condition, but experimental evidence is quantitatively conflicting in the case of clays (Wells, 1951; Willestts, 1954), and further work is in hand in the writer's laboratory to elucidate matters. Nothing in this section implies equivalence between soil water suction and a load applied mechanically in a specified direction.

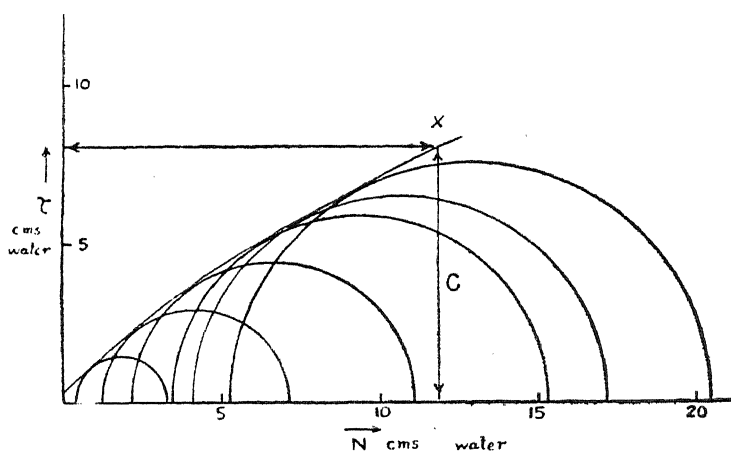


Fig. 2 Mohr's circles for sand, obtained by assuming the equivalence of pore water suction and externally applied pressure.

#### IV.—THE RELATIONSHIP BETWEEN VERTICAL LOAD AND PORE WATER PRESSURE IN SAND

The concept of the support of an applied load either by the soil particles or by the pore water may be illustrated by referring to sand, in which case no difficulties arise. Let us suppose that we have sand in a cylindrical vessel with a well fitting piston closing the upper end, the floor being either permeable to water or impermeable, at choice. The load is applied by means of the piston. We may distinguish several cases.

*Case 1. The floor of the vessel is impermeable, the sand is saturated, and the suction very slightly negative.*

The negative sign of the suction implies that there is a slight head of water standing above the surface of the sand. The piston clearly rests on the water and



is thereby kept off the sand. The piston load  $L$  is therefore transferred to the water, and the pore water pressure,  $u$ , is therefore given by

$$L = u \quad \dots \dots \dots (2)$$

The pressure is transmitted through the water to all walls of the vessel equally, and to the pore space, so that no load is carried by the sand and, in particular,  $L$  produces no additional tendency of the sand, considered as a column, to collapse. The wall therefore imposes, and experiences, no additional restraint pressure  $R$ , and performs no additional support function. In this case, since the suction is effectively zero, we have the rather trivial equation

$$L - u = s = 0$$

or  $u = L - s \quad \dots \dots \dots (3)$

It is this expression which we shall find to be freely used for clays when the suction is *not* zero.

*Case 2. The floor is impermeable, and the sand just less than saturated : the suction is very slightly positive.*

*Case 3. The floor is permeable and permits pore water to drain at zero hydrostatic pressure.*

These two cases may be taken together since, for different reasons, the pore water pressure,  $u$ , is zero. In case 2 the water surface is withdrawn very slightly below the sand surface and therefore cannot support the piston load, which is taken entirely by the sand particles, whilst in case 3 if the piston should act on the water, any attempt at compression causes the drainage of water through the permeable floor, the pressure being maintained at zero magnitude.

Hence  $s = 0$   
 $u = 0$

The load is taken by the sand, and equation (3) has no validity. If  $L$  is insufficient to cause collapse of the sand in the absence of the supporting vessel, no pressure is transferred to the walls. If  $L$  is large enough to cause the collapse of unsupported sand, then the wall pressure is given by  $R$  of equation (1). This difference of pressure on different surfaces in no way conflicts with the known isotropy and uniformity of fluid pressure in the pore space, for this fluid pressure is quite irrelevant to the wall and piston pressures.

*Case 4. The sand is saturated, but experiences the finite suction  $s$ , imposed, for example, via the permeable floor.*

By hypothesis,  $s$  is not sufficiently great to cause the entry of air into the pore space. This case is a development of case 3, and since the pore water pressure is quite unaffected by the load  $L$ , we have

$$u = -s$$

Again equation 3 has no validity. Since  $s$  is equivalent to an imposed external uniform pressure  $s$  in its effect on the strength of the sand, as outlined in section III, and is also additional to the applied vertical load  $L$ , collapse of unsupported sand would occur when, by an appropriate modification of equation 1,

$$R = s = (L + s) \tan^2 (\pi/4 + \phi/2) - 2c \tan (\pi/4 + \phi/2). \quad \dots \dots (4)$$

If  $L$  does not exceed this value, the wall pressure is zero. If  $L$  does exceed this value, then the walls must contribute a component  $P$  to the restraining pressure, such that

$$R = P + s = (L + s) \tan^2 (\pi/4 - \phi/2) - 2c \tan (\pi/4 - \phi/2). \dots (5).$$

The wall pressure is thus always less than  $L$ , the difference being greater the greater the suction.

#### V THE PRESSURE ON PLANES IN A SEMI-INFINITE SOIL

We shall consider a soil with a surface extending to infinity in all directions, and bearing a uniformly spread surface load, as for example in the case of large pavement and road surfaces. We shall consider the pressures on vertical and horizontal planes in this soil. The vertical load  $L$  on a given horizontal plane tends to cause collapse, and the soil on opposite sides of the vertical plane exerts mutual restraint  $R$ . It may well occur that the state of the soil is such that  $R$  is zero, as, for example, when the soil is seen to be deeply cracked. In this case the load  $L$  is clearly insufficient to cause collapse, since the cracks define unsupported "cliffs" of soil. In such a case  $R$  is zero. Another case corresponds to a load  $L$  which would cause collapse if the mutual restraint  $R$  were reduced (as, for example, by a slight horizontal shrinkage). The pressure on the vertical plane would then be given by  $P$  of equation (5), or  $R$  of equation (1) if the suction is zero (which would be rather rare in clay soils). If, on the other hand, the force  $R$  were not so much a restraint as a force of horizontal compression sufficient to lift the loaded surface, as, for example, if horizontal swelling after wetting could only be accommodated by a plastic distortion of this kind, then the roles of  $R$  and  $L$  would be reversed;  $R$  would be the load tending to produce soil collapse and  $L$  would be the restraint. In this case  $R$  would be much in excess of  $L$ . This latter case is not very likely in sands, which do not shrink and swell, but might occur in clays. Briefly, we may say that, because soils are not fluid, but can sustain a shear stress, pressure in soils is not isotropic, but may be different on planes in different directions.

#### VI. THE RELATIONSHIP BETWEEN VERTICAL LOAD AND PORE WATER PRESSURE IN CLAY

Clay differs from sand in that the particles are not in contact with each other until the soil water suction becomes very great. An increase of suction over the lower ranges causes a closer approach of the particles and a loss of water equivalent to the consequent reduction of volume. The case seems to be analogous to case 1 (for sand) in section IV, in that particles which are not in solid contact cannot support a surface load without reference to the intervening water. By analogy with case 1, the pore water is said to support the whole of the load  $L$ , the pore water pressure rising by an amount equal to  $L$ . Since, however, the suction of the pore water before the load is applied is not zero but  $s$ , the load does not increase the pore water pressure from zero to  $L$ , but reduces the suction from  $s$  to  $s-L$ . Hence

$$\begin{aligned} u &= -(s - L) \\ \text{or} \quad u &= L - s \dots \dots \dots (3) \end{aligned}$$

This is equation (3) generalised for finite suctions. There is, in this derivation, no discussion as to how the saturated clay is able to support a large suction; it is sufficient to say here that a plausible case may be made out on physical grounds for the validity of (3) when the load  $L$  is applied to a clay consisting of parallel



# THE CONCEPT OF DIFFUSION APPLIED TO SOIL WATER

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## SUMMARY

The development of the diffusion concept as applied to soil moisture movement is briefly reviewed. It is shown that the general differential equation describing isothermal liquid phase movement in a porous medium can be modified to include movement in the vapour and adsorbed phases as well, without complicating the mathematical form. A concentration-dependent diffusivity is derived which refers to movement in all three phases.

The significance and limitations of this equation in the study of hydrologic phenomena are discussed.

A derivation of the surface diffusivity of the absorbed phase for a highly idealized model is given in an appendix.

## I INTRODUCTION

"Either people were doubtful about the existence of such principles, or were doubtful about any success in finding them, or took no interest in thinking about them, or were oblivious to their practical importance when found" (Whitehead, 1926).

It is said to reflect that Alfred North Whitehead's description of the mediaeval attitude to the generalities of physical science might almost be from the mid-20th century chapter of some future history of the development of the principles of soil water movement.

The present communication is written in the belief that the principles *do* exist, *can* be found by wise experiment and intelligent theory, *are* interesting to think about and *are* of the greatest practical importance. It deals with the concept of diffusion as applied to soil moisture movement, indicating certain extensions of the concept as it is now usually understood and discussing certain of its limitations.

## II HISTORICAL

Two major steps in the development of a conceptual basis for the study of soil water movement were provided by Buckingham (1907), when he proposed

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the concepts of "capillary potential" and "capillary conductivity". The succeeding half-century has seen firstly the neglect and then the gradual re-discovery and exploration of the implications of Buckingham's work.

The "potential" concept gave information on the direction in which soil water movement might be expected and the "conductivity" expressed the proportionality between the potential gradient and the flow velocity. For a long time, however, the mathematical difficulties associated with the transient conditions most interesting to soil scientists and hydrologists seemed so great that the quantitative application of these concepts was limited to rather trivial steady state conditions.

The concept of diffusion was implicit in Buckingham's work and in that of Gardner and Widstoe (1921), but was first explicitly proposed by Childs (1936, *a*, *b*, 1938) and Nicholson and Childs (1936). Childs recognized the possibility of the diffusivity varying with moisture content, but the rather limited experimental evidence available led him to explore the (mathematically) simpler assumption of constant diffusivity.

This limited concept of diffusion was refuted in a paper by Kirkham and Feng (1949), which clearly showed that diffusion with constant diffusivity was not an acceptable model, a conclusion already reached by Childs and Collis-George (1948). It is important to emphasize that Kirkham and Feng's conclusions were reached about a model with *constant diffusivity*, since many people have quite mistakenly accepted this work as evidence that a diffusion model of soil water movement is inadmissible. Kirkham and Feng did, in fact state: "The differential equation of diffusion theory is not valid", but one must presume they were aware that they were using "diffusion" in its most limited (and quite needlessly restrictive) sense.

The concentration-dependent diffusivity was first derived by Childs and Collis-George (1948, 1950). This development implied the existence of a general partial differential equation describing water movement in the liquid phase in a porous medium which would prove to be of the diffusion type (*i.e.*, parabolic second order) when the pressure potential was a single valued function of the moisture content. It remained for this equation to be explicitly deduced and stated by Klute (1951 *a*, *b*).

### III MOVEMENT IN THE LIQUID PHASE

Equation (1) is Klute's equation recast with  $\theta$ , the moisture content expressed in volumetric terms and the liquid density assumed constant:

$$\frac{\partial \theta}{\partial t} = \nabla \cdot (K \nabla \phi) \quad (1)$$

$K$  is the permeability and  $\phi$  the total potential. This equation is applicable to any liquid but since our discussion is limited to the case when the liquid is water, it is convenient to take cm of water as the unit of potential and cm<sup>3</sup> per cm<sup>2</sup> per sec per unit potential gradient as the unit of permeability. The unit of time,  $t$ , is then the second.

Equation (1) may be converted to absolute form or made appropriate to any other liquid by a change of units and the introduction of the viscosity and surface tension of the liquid and the contact angle at the solid-liquid-gas line of contact (Philip, 1954 *a*).

When the total potential comprised purely gravitational and negative pressure (or capillary) components, as we shall assume throughout this paper, equation (1) may be rewritten

$$\frac{\partial \theta}{\partial t} = \nabla \cdot (K \nabla \Psi) + \frac{\partial K}{\partial \zeta} \quad (2)$$

Where  $\Psi$  is the pressure potential and  $\zeta$  is the vertical ordinate, positive upward.

When  $\Psi$  and  $K$  are single-valued functions of  $\theta$  (2) becomes

$$\frac{\partial \theta}{\partial t} = \nabla \cdot (D \nabla \theta) + \frac{\partial K}{\partial \zeta} \quad (3)$$

Where

$$D = K \frac{\partial \Psi}{\partial \theta} \quad (4)$$

#### IV POLYPHASE MOVEMENT

Let that portion of the moisture content of the porous medium held in the liquid phase be denoted  $\theta_{liq}$ , that portion in the vapour phase  $\theta_{vap}$ , and that portion held as absorbed films  $\theta_{ads}$ .

We now consider transport in the three phases. Let  $q_{liq}$ ,  $q_{vap}$ ,  $q_{ads}$  represent the flux in  $\text{cm}^3$  per  $\text{cm}^2$  per sec in the respective phases. Then, from Darcy's Law

$$q_{liq} = -K \nabla \Psi \quad (5)$$

or alternatively

$$q_{liq} = -D_{liq} \nabla \theta - K i \quad (6)$$

Where  $D_{liq} = K \partial \Psi / \partial \theta$  (and is equivalent to  $D$  employed in the previous section) and  $i$  is a unit vector in the upward vertical direction.

Now the equation for water-vapour diffusion in a non-turbulent free atmosphere.

$$q_{vap} = -D_{atm} \nabla \rho \quad (7)$$

where  $\rho$  is the density of water vapour and  $D_{atm}$  the diffusivity of water vapour in air) must be modified by a tortuosity factor  $a$  and allowance made for the variability with  $\theta$  of the cross-section available for diffusion. The result is (8) :

$$q_{vap} = -a(p - \theta) D_{atm} \nabla \rho \quad (8)$$

where  $p$  is the porosity of the medium. The error in (8) incurred in writing  $(p - \theta)$  for the fractional cross-sectional area available for diffusion rather than the more correct  $(p + \theta_{vap} - \theta)$  is of the order of 1 in  $10^5$  in the humidity and temperature range which concerns us here.

Penman (1940 *a, b*) suggests  $a = 0.66$ . Later work by van Bavel (1952) leads to  $a = 0.58$ . Flegg (1950) confirms that  $a$  is of this order of magnitude and is sensibly independent of  $(p - \theta)$  in the range which is relevant to soil water studies. None of these workers used water vapour as the diffusing substance. Some limited and incomplete experiments of the author's suggest that (8) holds also for water vapour, at least under isothermal conditions.

Thermodynamic considerations (*vide*, for example, Edlefsen and Anderson, 1943) give the relationship

$$\rho = \rho_0 e^{\psi g / RT} \quad (9)$$

where  $\rho_0$  is the saturated vapour density,  $g$  the acceleration due to gravity,  $R$  the gas constant per gram of water vapour and  $T$  the absolute temperature.

$$\text{Therefore } \frac{\partial \rho}{\partial \theta} = \frac{\rho_0 g}{RT} e^{\psi g / RT} \frac{\partial \psi}{\partial \theta} \quad (10)$$

use of this equation in (8) gives

$$q_{vap} = - \frac{\rho_0 g}{RT} \alpha(p-\theta) D_{atm} e^{\psi g / RT} \frac{\partial \psi}{\partial \theta} \quad (11)$$

$$\text{or } q_{vap} = - D_{vap} \nabla \theta \quad (12)$$

$$\text{where } D_{vap} = \frac{\rho_0 g}{RT} \alpha(p-\theta) D_{atm} e^{\psi g / RT} \frac{\partial \psi}{\partial \theta} \quad (13)$$

Thus when  $\psi$  is a known function of  $\theta$  and  $T$  is fixed,  $D_{vap}$  may be determined as a function of  $\theta$ .

Babbitt (1950) has investigated theoretically the surface diffusivity of adsorbed films. He deduced that the diffusivity was concentration dependent. From a very different standpoint the author has examined the case of surface diffusion in the ideal two-dimensional gas (de Boer 1953) admittedly a highly idealized model of adsorption which can only be of very limited applicability to soil water systems. The result, given in Appendix I, is once more a surface diffusivity which is concentration-dependent.

The precise form of this dependence is unimportant for our present purpose. It suffices that movement in the adsorbed phase can be described by an equation of the form

$$q_{ads} = - D_{ads} \nabla \theta \quad (14)$$

Then, summing equations (6), (12) and (14), we have

$$q = - D \nabla \theta - K \dot{\theta} \quad (15)$$

$$\text{where } D = D_{liq} + D_{vap} + D_{ads} \quad (16)$$

Applying the requirements of continuity to equation (15) we obtain

$$\begin{aligned} \frac{\partial \theta}{\partial t} &= \nabla \cdot (D \nabla \theta + K \dot{\theta}) \\ \text{i. e. } \frac{\partial \theta}{\partial t} &= \nabla \cdot (D \nabla \theta) + \frac{\partial K}{\partial z} \end{aligned} \quad (17)$$

It will be noted that equation (17) is identical with equation (3). The sole difference is that our new  $D$ , also a function of  $\theta$ , is such that vapour and adsorbed phase movements are taken into account as well as liquid phase movements. Thus the new equation enables the treatment of polyphase movement without adding to the mathematical complication.

It is of interest to consider the general shape of the diffusivity function. Fig. 1 shows the  $\psi$ - $\theta$  and  $K$ - $\theta$  curves for a soil, based on the data of Moore (1939) for Yolo light clay but extrapolated to lower moisture contents on the basis of other data and the method of permeability computation due to Childs and Collis-George (1950). Fig. 2 shows the  $D_{liq}$ ,  $D_{vap}$  and  $D^1$  (taken as  $[D_{liq} + D_{vap}]$ ) curves for the soil characterized by Fig. 1.  $D$  is neglected because no reliable estimate can be made; it seems probable that  $D^1$  will not vary greatly from  $D$  except for very dry soils of high specific surface. For computing  $D_{vap}$ ,

the temperature was taken as 20°C,  $\alpha$  as 0.6 and  $p$  as 0.495, the value determined by Moore (1939).

It will be observed that  $D^1$  falls to a minimum as  $\theta$  diminishes and then rises to a secondary peak. The exact values of  $\theta$  and  $D$  at this minimum are uncertain since experimental values of  $K$  in this region are not available. However, it is clear that  $K$  falls to zero at some finite moisture content,  $\theta_k$ , at which continuity of the liquid phase ceases and that this almost certainly occurs at moisture contents greater than that corresponding to the maximum of the  $D_{vap}$  curve. Thus  $D^1$  will attain its minimum value when  $\theta$  is somewhat greater than  $\theta_k$ .

Staple and Lehane (1954) have observed a  $D-\theta$  relationship of this shape. The data of Buckingham (1907) is also consistent with this shape of curve. The shape of the  $D_{vap}$  curve may account for the frequent observation (Gurr *et al*, 1952, which includes further references) that there is a distinct optimum for vapour transfer occurring at low moisture contents, the rate of transfer falling to zero as  $\theta$  either decreases to zero or increases to saturation.

## V. APPLICATION TO HYDROLOGIC PHENOMENA

If equation (17) is valid, then the many problems of interest to the soil physicist and hydrologist (such as infiltration, drainage, evaporation from soils, wilting point) are described by solutions of the equation for the appropriate initial and boundary conditions.

Because the  $D$  and  $K$  functions cannot be represented adequately by analytic functions, formal mathematical methods are impossible and numerical and mechanical methods must be used to solve problems. In fact even if  $D$  and  $K$  could be represented algebraically, the complexity of (17) would still be such that numerical methods would almost certainly still be needed for all but the simplest conditions.

Numerical methods are being developed to enable the exploration of this line of approach and some interesting results have already been obtained which have shed light on the physics of infiltration and evaporation from soils (Philip, 1954b, provides a preliminary report. It is hoped to report this work more fully elsewhere).

## VI. SOME LIMITATIONS

The approach described in this communication may not be valid when there is not a unique functional relation between  $\theta$  and  $\psi$ . A few cases of real or apparent difficulty are discussed below:

(a) For the range of values of  $\psi$ , zero to  $\psi_0$ , where  $\psi_0$  is the "air entry value" of the medium, the requirement that  $\psi$  is a unique function of  $\theta$  is not met. However, since  $\theta$  remains uniquely determined for each value of  $\psi$ , it is possible to rewrite equation (2):

$$F \frac{\partial \psi}{\partial t} = \nabla (K \nabla \psi) + \frac{\partial K}{\partial \psi} \quad (18)$$

where  $\frac{\partial}{\partial \psi} (\psi) = \frac{\partial \theta}{\partial \psi}$  and  $K = K(\psi)$

In this form the equation represents the diffusion of potential, *not* of liquid. For polyphase movement  $K$  in the first term of the right hand side of (18) must be replaced by  $[K + F(D_{liq} - D_{vap})]$



(b) If overburden pressure,  $P$ , influences porosity and total potential, so that

$$\psi = \psi(\theta, P) \quad (19)$$

the  $\psi$ - $\theta$  relation is not unique. This limitation will be most important in deep soils of high colloid content when  $\theta$  is fairly high.

(c) Before a soil pore can be filled during wetting up, it is necessary that the original air in the pore have a free passage to the atmosphere. However, if the pore is larger than all the surrounding pores, they will fill with water first, air will be entrapped in the pore we are considering and the pore will remain unfilled. Obviously the chance that the air in any pore will be unable to escape will increase with  $l$ , the distance the pore is from the surface of the soil mass, so we may then write

$$\theta = \theta(\psi, l) \quad (20)$$

and the  $\psi$ - $\theta$  relation is not unique. There is some evidence from the data of Bodman and Colman (1944) that for  $l$  greater than 2 to 3 cm this effect is unimportant even in the most aggravated case which would occur when there is free water at the surface.

(d) Contrary to what one might expect, the hysteresis phenomenon first reported by Haines (1930) introduces no difficulty provided the part of the hysteresis loop used as the  $\psi$ - $\theta$  curve is appropriate to the phenomenon.

A difficulty does arise, however, in the drainage of soil columns, when at any point in the soil  $\theta$  may initially increase with time and then finally decrease with time. One might have thought that by adopting "wetting" and "drying" diffusivities, to be applied according to the sign of  $\partial\theta/\partial t$ , the difficulty would be overcome. I am indebted to Dr. E. C. Childs for pointing out in discussion the inadequacy of such an approach. If one reflects that points on either side of the point at which  $\partial\theta/\partial\psi = 0$  will be on different parts of the hysteresis loop and  $\frac{\partial\psi}{\partial\theta}$  at the point ceases to be a unique function of  $\theta$  i.e., the phenomenon ceases to be one of diffusion, since any "diffusivity" one might derive becomes a function not only of  $\theta$  but also of the manner in which  $\theta$  is varying with  $x$  and  $t$ .

(e)  $K$  may vary with electrolyte concentration in soils of high colloid content, so that the conditions are not satisfied when gradients of electrolyte concentration exist in soils of this type.

In addition, it is emphasized that the treatment in this communication deals with isothermal conditions in homogeneous soils.

Despite this formidable array of limitations, the concepts outlined in this paper offer a theoretical framework capable of application to a wide range of soil moisture phenomena. Exploration of the implications of this approach seems a logical step towards the understanding of the diverse phenomena confronting the soil physicist and hydrologist.

## VII. ACKNOWLEDGMENT

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## APPENDIX I

### DERIVATION OF SURFACE DIFFUSIVITY IN THE IDEAL TWO-DIMENSIONAL GAS

For an ideal two-dimensional gas (de Boer, 1953) with negligibly small energy of activation for surface migration, the chance of a molecule colliding with another whilst moving through the space interval  $x$  to  $(x+\delta x)$  is

$$2 N a \delta x$$

where  $N$  is the number of molecules per unit area and  $a$  is the molecular diameter.

If  $\frac{dN}{dx} = n$  and  $N = N_0$  at  $x = 0$ , and  $\omega$  is the chance that a molecule will not collide with another before it has travelled a free path  $x$ ,

$$\delta \omega = 2 a \omega (N_0 + n x) \delta x$$

$$\text{i.e.} \quad \frac{d\omega}{dx} = 2 a \omega (N_0 + n x)$$

Integration gives

$$\omega = e^{-2 a N_0 x (1 + \frac{n}{2 N_0} x)}$$

The mean free path of molecules moving in the positive direction will therefore be

$$\int_0^{\infty} \omega dx, \quad \text{i.e.} \quad \int_0^{\infty} e^{-2 N_0 x (1 + \frac{n}{2 N_0} x)} dx$$

$$\text{i.e.} \quad \int_0^{\infty} e^{-2 a N_0 x \left( 1 - a n x^2 + \frac{(a n x^2)^2}{2!} - \frac{(a n x^2)^3}{3!} + \dots \right)} dx$$

Evaluating the definite integral, we obtain

$$\frac{1}{2 a N_0} \left( 1 - \frac{2! a n}{1! (2 a N_0)^2} + \frac{4! (a n)^2}{2! (2 a N_0)^4} - \frac{6! (a n)^3}{3! (2 a N_0)^6} + \dots \right)$$

which can be reduced to

$$\frac{1}{2 a N_0} \left( 1 - \frac{2!}{1!} \left( \frac{n}{4 a N_0^2} \right) + \frac{4!}{2!} \left( \frac{n}{4 a N_0^2} \right)^2 - \frac{6!}{3!} \left( \frac{n}{4 a N_0^2} \right)^3 + \dots \right)$$

Since  $N_0^2$  will generally be large in comparison to  $n/a$  we may neglect terms of higher order than the first, giving

$$\frac{1}{2 a N_0} \left( 1 - \frac{n}{2 a N_0^2} \right)$$

Now if  $v$  is the value of  $n$  in the direction of maximum positive concentration gradient,  $n = v \cos \gamma$ , where  $\gamma$  is the angle the direction  $x$  makes with this direction.

Thus the mean free path of a molecule crossing the line  $N = N_0$  is

$$\frac{1}{2 a N_0} \left( 1 - \frac{v \cos \gamma}{2 a N_0^2} \right)$$

and is obviously a function of its direction of travel. But the direction of movement of the molecules is random, so that any value of  $\gamma$  from 0 to  $2\pi$  is as likely as any other. Thus the vectorially averaged mean free path equals

$$\frac{1}{2 a N_0} \int_0^{2\pi} \left( 1 - \frac{v \cos \gamma}{2 a N_0^2} \right) \cos \gamma d\gamma \bigg/ \int_0^{2\pi} d\gamma$$

Which reduces to

$$\frac{v}{8 a^2 N_0^3}$$

in the direction of the greatest *negative* concentration gradient, i.e., in the direction  $\gamma = \pi$ .

Now if the mean velocity of the molecules is  $c$  cm. sec<sup>-1</sup>, the vectorially averaged velocity will be

$$\left( -\frac{v}{8 a^2 N_0^3} \right) \cdot c$$

$$\text{i.e., } -\frac{vc}{4 a N_0^2} \text{ cm. sec}^{-1}$$

Therefore the nett flux density normal to the line  $N = N_0$

$$\text{is } \frac{vc}{4 a N_0} \text{ molecules cm.}^{-1} \text{ sec}^{-1}$$

The ratio of the flux to the concentration gradient  $v$  is the surface diffusivity

$$\frac{C}{4 a N_0} \text{ cm}^2 \text{ sec}^{-1}$$

$$\text{or } \frac{\pi a c}{16 \bar{\epsilon}} \text{ cm}^2 \text{ sec}^{-1}$$

where  $\bar{\epsilon}$  is the density of adsorption in statistical monolayers.

Therefore

$$q_{ads} = - \frac{A \beta \pi a c}{16 \bar{\epsilon}} \nabla \bar{\epsilon}$$

Where  $A$  is the surface area of the medium in cm<sup>2</sup>/cm<sup>3</sup> and  $\beta$  is a "tortuosity factor".

Whence

$$q_{ads} = - \frac{A \beta \pi a c}{16 \bar{\epsilon}} \frac{\partial \bar{\epsilon}}{\partial \theta} \nabla \theta$$

Comparing this equation with equation (14), we observe that for this model of surface diffusion,

$$D_{ads} = \frac{A \beta \pi a c}{16 \epsilon} \frac{\partial \epsilon}{\partial \theta}$$

$\epsilon$  is a function of  $\theta$ , so that  $D_{ads}$  is also a function of  $\theta$ .

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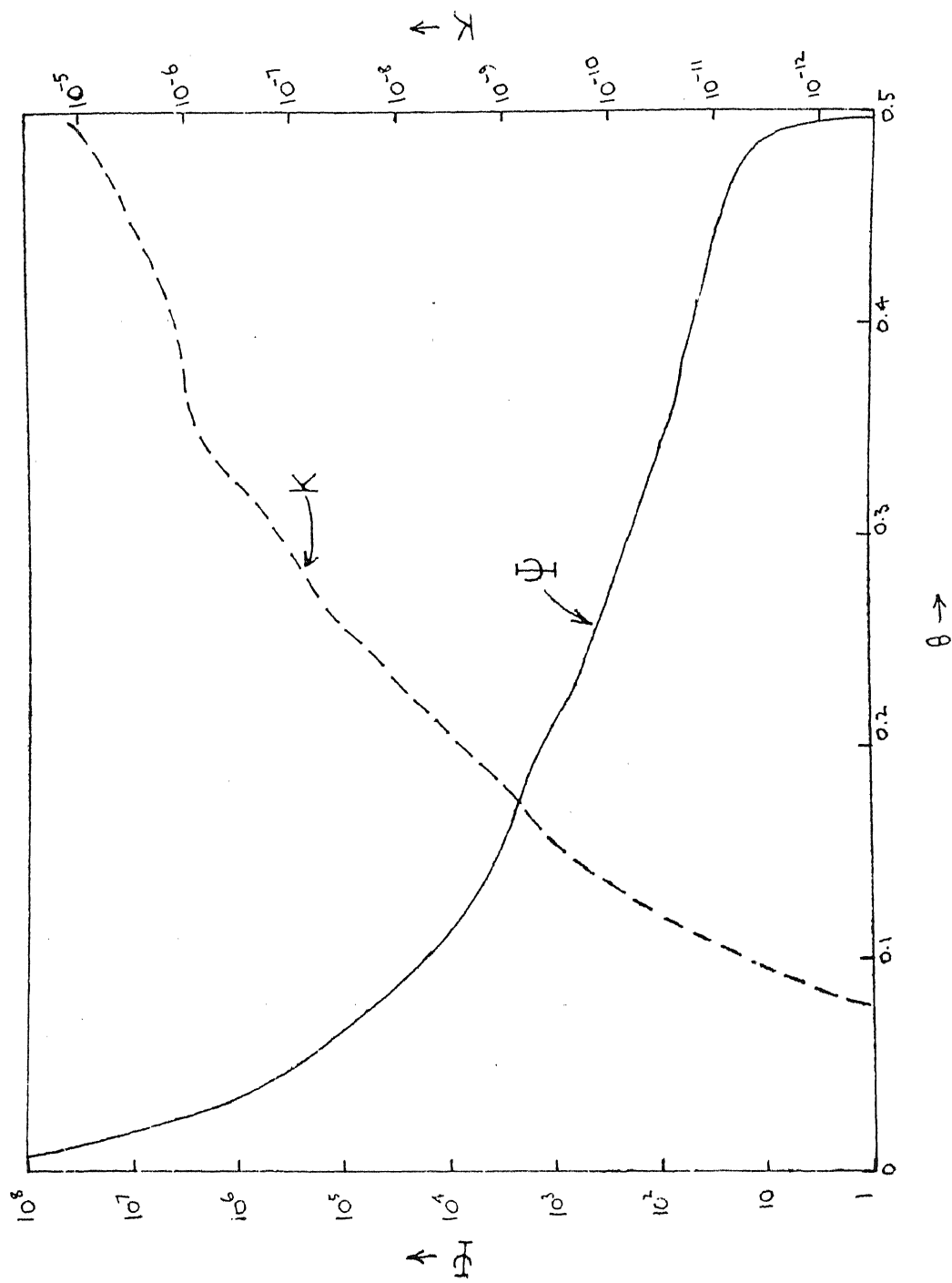


Figure 1. Typical  $K$ - $\theta$  and  $\Psi$ - $\theta$  curves.

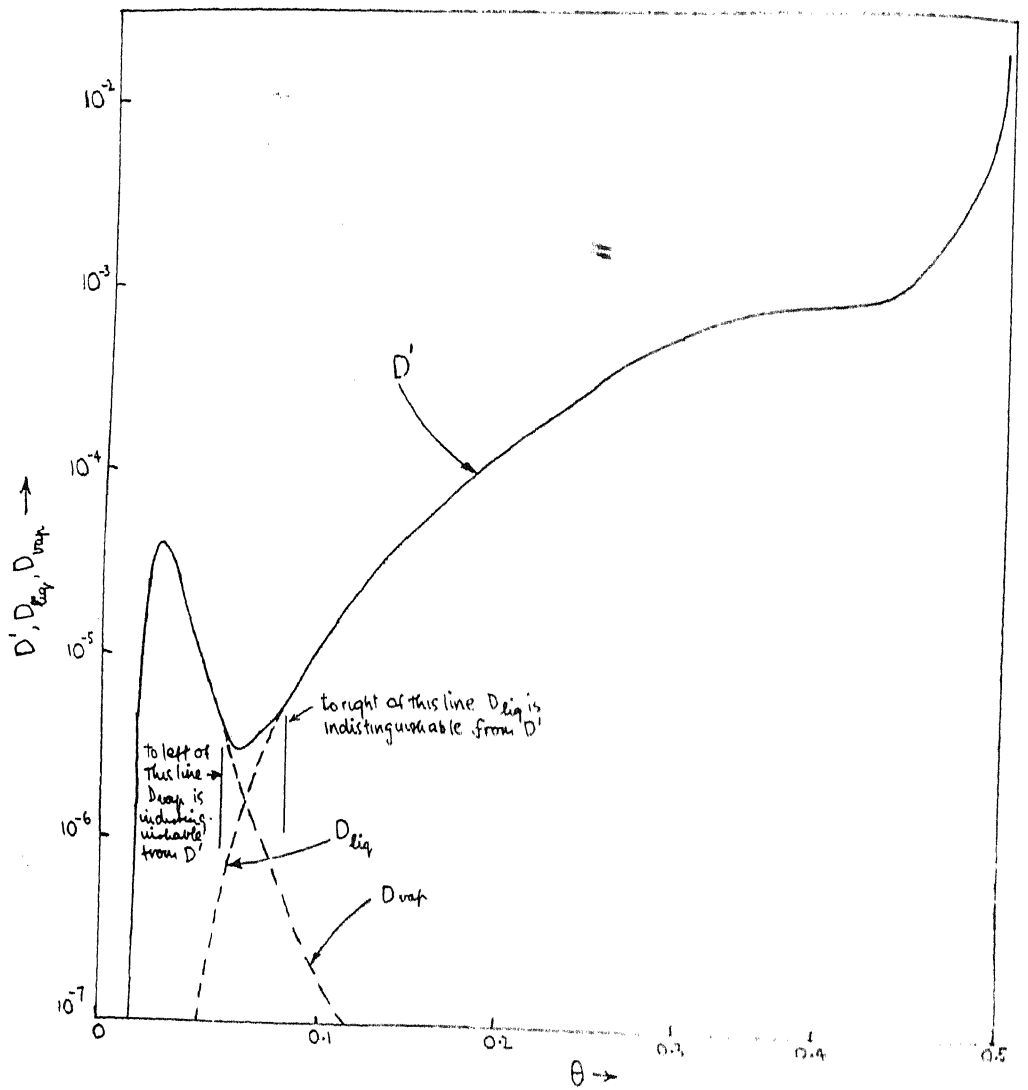


Figure 2.  $D_{liq}$ ,  $D_{vap}$  and  $D'$  curves computed from the data of Figure 1.